PB86-100591

Introduction to Ground-Water Tracers

Arizona Univ., Tucson

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

Mar 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-100591

EPA/600/2-85/022
March 1985

AN INTRODUCTION TO GROUND-WATER TRACERS

by

Stanley N. Davis
Darcy J. Campbell
Harold W. Bentley
Timothy J. Flynn
Department of Hydrology and Water Resources
University of Arizona
Tucson, Arizona 85721

Cooperative Agreement CR-810036

Project Officer
Jerry Thornhill
Robert S. Kerr Environmental Research Laboratory
Ada, Oklahoma 74820

ROBERT S. KERR ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ADA, OKLAHOMA 74820

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-85/022	2.	3. RECIPIENT'S ACCESSION NO. PB86 100591/AS
4. TITLE AND SUBTITLE An Introduction to Ground-Water Tracers		5. REPORT DATE March 1985
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Stanley N. Davis, Darcy J. Campbell, Harold W. Bentley, and Timothy J. Flynn		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Hydrology and Water Resources University of Arizona Tucson, Arizona 85721		10. PROGRAM ELEMENT NO. CBPC1A
		11. CONTRACT/GRANT NO. CR-810036
12. SPONSORING AGENCY NAME AND ADDRESS U.S. EPA Robert S. Kerr Environmental Research Laboratory P.O. Box 1198 Ada, OK 74820		13. TYPE OF REPORT AND PERIOD COVERED Final Report 9/82 to 12/84
		14. SPONSORING AGENCY CODE EPA-600/15
15. SUPPLEMENTARY NOTES EPA Project Officer - Jerry T. Thornhill, FTS 743-2310		

16. ABSTRACT

The general field of ground-water tracers is introduced along with some basic hydrogeologic principles used in planning and conducting tracer tests. The final chapter describes tracer types by category and provides information on specific field techniques, detection limits, laboratory analysis, etc.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ground water Darcy's Law Water table Recharge Wells	Tracers	68D

18. DISTRIBUTION STATEMENT Release to public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 216
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques, and new technologies through which optimum use of the nation's land and water resources can be assured and the threat which pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated zone and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

This report contributes to that knowledge which is essential in order for EPA to establish and enforce pollution control standards which are reasonable, cost effective, and provide adequate environmental protection for the American public.

Clinton W. Hall

Clinton W. Hall
Director
Robert S. Kerr Environmental
Research Laboratory

CONTENTS

Page

- Foreword iii
- Abstract vii
- Preface ix
- Figures x
- Tables xii
- Acknowledgments xiii

- Chapter 1 1
  - Introduction 1
    - General characteristics of tracers 1
    - History of ground-water tracing 2
    - Purpose and scope 3
    - Public health considerations 5

- Chapter 2 7
  - Hydrogeologic principles 7
    - Darcy's law 7
    - Direction of water movement 11
    - Travel time 14
    - Sorption of tracers and related phenomena 14
    - Hydrodynamic dispersion and molecular diffusion 18

- Chapter 3 21
  - Practical aspects 21
    - Planning a test 21
    - Types of tracer tests 24
      - Single-well techniques 26
        - Injection/withdrawal 26
        - Borehole dilution 34
      - Two-well techniques 36
        - Uniform flow 36
        - Radial flow 37
    - Design and construction of test wells 38
    - Injection and sample collection 43
    - Interpretation of results 47

- Chapter 4 57
  - Types of tracers 57
    - Temperature 57
      - Field methods 61
      - Detection and analysis 61
      - Additional information 62
    - Solid particles 62
      - Paper and simple floats 63
        - Field methods 63
        - Detection 63
        - Additional information 63
      - Signal-emitting floats 64

Page

Yeast 64
  Field methods. 65
  Detection. 65
  Additional information 65
Bacteria. 67
  Field methods. 68
  Detection. 68
  Additional information 68
Viruses 69
  Field methods. 72
  Additional information 73
Spores. 74
  Field methods. 75
  Detection and analysis 77
  Additional information 79
Ions. 82
  Field methods. 84
  Detection and analysis 87
  Discussion of specific ion tracers 89
    Chloride. 89
    Bromide 90
    Lithium 92
    Ammonium. 92
    Magnesium 92
    Potassium 92
    Iodide. 92
    Organic anions. 92
Dyes. 93
  Field methods. 96
  Detection and analysis 98
  Additional information 99
  Discussion of specific dye tracers 106
    Green dyes. 106
      Fluorescein. 106
      Pyranine 109
      Lissamine FF 109
    Orange dyes 109
      Rhodamine B. 109
      Rhodamine WT 110
      Sulfo rhodamine B. 114
    Blue dyes 114
Some common nonionized and poorly ionized compounds 115
  Detection. 117
Gases 117
  Introduction 117
  Inert Radioactive Gases. 118
  Inert Natural Gases. 118
  Fluorocarbons. 120

Page

Field Methods. 122
Analysis 125
Stable isotopes 125
Introduction 125
Hydrogen and oxygen. 126
Nitrogen 127
Sulfur 130
Carbon 130
Isotopes of other elements 131
Field methods. 131
Analysis 133
Radionuclides 133
Introduction 133
Injected tracers 134
Atmospherically distributed radionuclides. 138
Field methods. 143
Analysis 144

Appendixes

Appendix A. 145
Additional uses of water tracers 145
Appendix B. 150
A discussion of dispersion and diffusion 150
Appendix C. 159
Factors to consider in tracer selection. 159
Appendix D. 165
Chemical supply companies. 165
Appendix E. 169
Analytical methods for the detection of tracers. 169
References 182

ABSTRACT

The general field of ground-water tracers is introduced with an effort to present current techniques and knowledge. Some basic hydrogeologic principles used in planning and conducting tracer tests are presented in the second chapter. Various types of tests and practical considerations related to well design, injection and sampling of the tracer, and interpretation of results are discussed in Chapter 3. The final chapter describes tracer types by category (e.g., dyes, ions, stable isotopes) and provides information on specific field techniques, detection limits, laboratory analysis, etc. Numerous references to actual tracer tests are provided for each tracer type, and some of the positive and negative aspects of each tracer type are discussed.

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under cooperative agreement CR-81003601-0 to the University of Arizona. It has been subject to the Agency's peer and administrative review and it has been approved for publication as an EPA document.

PREFACE

An Introduction to Ground-Water Tracers has been developed in conjunction with the U.S. Environmental Protection Agency for use by persons involved in efforts to determine the direction and velocity of ground-water flow. Techniques described are those which are currently in use and methods which may be of future significance.

For those concerned with protecting ground water, this document may be helpful as a ready summary of methods to determine the movement of ground water and contaminants in an aquifer.

FIGURES

Page

2.1 Darcy's Law 8

2.2 Direction of water movement 12

2.3 Divergence from regional direction of water movement. 13

2.4 Average travel time of ground water 15

2.5 Hydrodynamic dispersion 19

2.6 Molecular diffusion 20

3.1 Slope of the water table. 23

3.2 Tracer tests at Sand Ridge State Forest, Illinois 25

3.3 Different arrangements for ground-water tracing 27

3.4 Tracer test in alluvium 40

3.5 Two-well tracer test in fractured rock. 41

3.6 Tracer test using water temperature 44

3.7 Variation of chemical quality with time 46

3.8 Arrival of tracer front 48

3.9 Dispersion in breakthrough curves 50

3.10 Incomplete saturation of aquifer. 51

3.11 Conservative vs. nonconservative tracers. 53

3.12 Computer-generated type curves. 56

4.1 Results of tracer test using hot water. 60

4.2 Results of two-well tracer tests using bromide and yeast 66

4.3 Two-well tracer test using rhodamine WT and E. Coli 70

4.4 Use of plankton net to catch spores 78

Page

4.5 Comparison of tracer pulse from lycopodium spores and a dye in a karst system 80

4.6 Comparison of several tracers in a laboratory test. 91

4.7 Excitation and emission characteristics of rhodamine WT. 95

4.8 Automatic monitoring system for a stream. 100

4.9 Effect of pH on fluorescence. 102

4.10 Adsorption of dyes on kaolinite 103

4.11 Comparison of travel time for lycopodium spores, hot water, and fluorescein. 105

4.12 Arrival times of tritium and rhodamine WT in a field test. 112

4.13a Laboratory experiments with fluorocarbon tracers 123

4.13b Tracer elution curves for NaCl and CCl_3F 124

4.14 Relation between oxygen-18 and deuterium for natural waters. 128

4.15 Oxygen-18 variations in ground water of the Tucson basin. 129

4.16 Carbon isotopes in methane. 132

4.17 Local direction of ground-water movement using radioactive tracers 137

4.18 Average annual tritium concentration of rainfall and snow. 141

TABLES

Page

2.1 Representative values of porosity, hydraulic conductivity, and permeability. 10

4.1 Comparison of microbial tracers 71

4.2 Comparison of lycopodium and fluorescent dye properties. 81

4.3 Analytical methods for ionic tracers. 88

4.4 Description of dye tracers. 94

4.5 Sensitivity and minimum detectable concentrations of dye tracers. 101

4.6 Relative costs of dyes. 107

4.7 Sorption of dyes on bentonite 113

4.8 Compounds soluble in water. 116

4.9 Gases of potential interest as tracers. 119

4.10 Properties of fluorocarbon compounds. 121

4.11 Commonly used radioactive tracers 135

4.12 Environmental radionuclides 139

B.1 Values of dispersivities measured by various methods 156

Acknowledgments: Mr. Jack Keeley of the Robert S. Kerr Environmental Research Laboratory encouraged us in launching the initial project. Drs. Glenn M. Thompson and Emanuel Mazor gave valuable direction in the initial stages of the work. Much of the library research was done by Michael G. Wallace. Drafting was completed by Ms. Ann Cotgageorge and manuscript typing was done by Ms. Corla Thies. Field assistance in conducting tracer tests was provided by Jesus Carrera and Morley Weitzman. To these individuals and others who have helped us, we are grateful.

CHAPTER ONE

INTRODUCTION

General Characteristics of Tracers

As used in hydrogeology, a tracer is matter or energy carried by ground water which will give information concerning the direction of movement and/or velocity of the water and potential contaminants which might be transported by the water. If enough information is collected, the study of tracers can also help with the determination of hydraulic conductivity, porosity, dispersivity, chemical distribution coefficients, and other hydrogeologic parameters. A tracer can be entirely natural, such as the heat carried by hot-spring waters; it can be accidentally introduced, such as fuel oil from a ruptured storage tank; or it can be introduced intentionally, such as dyes placed in water flowing within limestone caverns (Davis et al., 1980).

A tracer should have a number of properties in order to be generally useful. The most important criterion is that the potential chemical and physical behavior of the tracer in ground water must be understood. The objective is commonly to use a tracer which travels with the same velocity and direction as the water and does not interact with solid material. For most uses, a tracer should be nontoxic. It should be relatively inexpensive to use and should be, for most practical problems, easily detected with widely available and simple technology. The tracer should be present in concentrations well above back-ground concentrations of the same constituent in the natural system which is being studied. Finally, the tracer itself should not modify the hydraulic conductivity or other properties of the medium being studied.

Obviously, an ideal tracer does not exist. Because of the complexities of the natural systems which are studied, together with the large number of requirements for the tracers themselves, the selection and use of tracers is almost as much of an art as it is a science. This manual will describe some of this art and also explain some of the important scientific principles needed to apply the art effectively.

History of Ground-Water Tracing

One of the first tracing experiments was performed almost 2,000 years ago when Philip, the tetrarch of Trachonitis, threw chaff into a crater lake. He reported that the chaff appeared down gradient in one of the springs at the headwaters of the Jordan River. Although Josephus reported that the experiment was a success, Mazor (1976) demonstrated by chemical and isotopic measurements that the supposed underground connection would be highly unlikely. Around the same period of time, Strabo described karst tracing experiments (Burden, 1963). The karst areas of Europe abound with folk legends of cavern connections demonstrated by straying ducks and dogs (Brown and Ford, 1971).

Dyes and salts have been used in Europe since 1869 to find hydraulic connections in karst areas (Kass, 1964). Among the first dye experiments was an effort made to establish the water origin of typhoid fever in France in 1882. Dole (1906) mentioned the work of Dr. Carrieres during this severe epidemic near Paris. The fluoroscope was invented in France in 1901 by M. Trillat and perfected by M. Marboutin. This instrument greatly increased the precision of fluorescent dye measurements. Dole described work in France with karst and soil tracing and pioneered the use of fluorescein in English-speaking countries.

During the same time, Thiem used sodium chloride in investigations in Leipzig to determine the flow velocity of water (Slichter, 1902). Thiem sampled for chloride, which he analyzed in the laboratory. Slichter modified Thiem's method by obtaining continuous recordings of electrical conductivity in the field. Ammonium chloride was used in Schlicter's experiments. Slichter (1905) also determined time of travel and direction of flow in perhaps the first field tracer tests in porous media. His use of shallow drive point wells and resistivity measurement was modified by the authors of this manual, and was used in small-scale field tests described in a subsequent chapter.

In the 1950's, radioactive tracers were developed (Fox, 1952), allowing very precise and selective tracer measurement. They were quite popular, although their use has been curtailed in many countries for public health reasons. In the 1960's, naturally occurring radioisotopes and stable isotopes became an invaluable tracing tool. In the last two decades, researchers have developed extremely sensitive tracers, including fluorinated organic acids and halocarbons.

Purpose and Scope

The purpose of this manual is to provide a guide to the use of ground-water tracers for practicing engineers, hydrologists, and ground-water geologists. Some parts of the manual may prove to be useful to research scientists, however, emphasis has been placed on the practical rather than on the theoretical aspects of tracers. Specifically, the manual is concerned with the selection of tracers, their field application, collection of samples containing tracers, sample analysis, and interpretation of the results.

Only a general introduction will be provided, however, to laboratory analyses and quantitative interpretation of the results.

The number of possible tracers which can be used in ground water must number in the thousands, if all trace constituents together with stable isotopes and radionuclides are considered. In this manual, emphasis has been placed on the more practical tracers, while several other tracers have been mentioned which may be used for special applications. References given in the bibliography will cover a large number of additional tracers which are not discussed in detail in the manual.

Except for volatile tracers and tracers which break down in sunlight, ground-water tracers can be used for surface-water work. The reverse is not always true. One of the most common errors in ground-water tracer work is to use dyes which have been applied successfully in surface-water studies. Many excellent studies of surface-water tracers are available, but cannot be used directly for ground-water work. This manual is intended for people interested in ground-water tracing; thus, many of the limitations of surface-water tracers as applied to subsurface problems have been pointed out.

While some space has been given to natural tracers and tracers introduced accidentally through pollution, most of the manual is focused on material injected intentionally into ground water for the purpose of tracing the movement of fluids in active ground-water systems. Tracer applications in the petroleum industry are mentioned in Appendix A.

The purpose and importance of tracer tests was eloquently described by Dole (1906), and his sentiments are consistent with the philosophy of this manual.

> "Consequently, every means for determining the flow and pollution foci of underground waters should be used. In studying the potability of a well or spring water, it is important to know not only its chemical composition, but also its source, its rate of flow, the area tributary to it, the nature of the material through which it passes, and the contaminations to which it may be subjected before or during its underground journey. It is often a matter of much importance to know whether the flow is from a cesspool toward a neighboring well or in the opposite direction; it may be necessary to determine whether or not water seeps from a contaminated brook into wells of a neighboring region; whether collecting galleries for public water supplies receive seepage from well-established sources of contamination; whether, in general, known foci of pollution are in immediate, though obscured, connection with sources of drinking water. Knowledge of this nature is especially important in the study of waters passing through formations full of seams or crevices, where there is opportunity for rapid circulation without much purification. The determination of the area draining to the underground supply affords data in regard to the quantity of available water as well as its quality."

Public Health Considerations

Tracers discussed in detail in this manual are mostly harmless and should pose no public health problems. One cannot emphasize too strongly, however, that each artificial introduction of tracers must be done with a careful consideration of possible health implications. Commonly, investigations using artificially introduced tracers must have the approval of local or state health authorities, local citizens must be informed of the tracer injections, and the results should be made available to the public. In addition, under some circumstances, analytical work associated with tracer studies must be done in appropriately certified laboratories. Because of the extreme variability of local and state regulations and because of the rapid changes in these regulations, it is impractical to include an extensive discussion of public health aspects of tracers. Therefore, the authors disclaim any responsibility for judging the health effects of the tracers covered in this manual.

CHAPTER TWO

HYDROGEOLOGICAL PRINCIPLES

The following discussion is intended only as a brief introduction to some of the hydrogeological principles necessary for the application of tracer technology. More complete information can be found in standard textbooks on the topic (Bouwer, 1978; Davis and DeWiest, 1966; Fetter, 1980; Freeze and Cherry, 1979; Heath and Trainer, 1968; and U.S. Bureau of Reclamation, 1977).

Darcy's Law

Most ground-water flow is governed by Darcy's law, which must be understood in order to design successful tracer tests. For a simple flow system, Darcy's law states that the volume of water flowing per unit of time, Q, through a given cross section, A, is directly proportional to the hydraulic gradient, $\frac{\Delta h}{\Delta L}$, and the hydraulic conductivity, K. Stated as an equation, this is:

$$Q = KA \frac{\Delta h}{\Delta L} \qquad (1)$$

The meaning of this equation is illustrated by Figure 2.1.

The hydraulic conductivity, K, is in itself a complex measure of a number of physical factors. One useful equation relating these factors is:

$$K = d^2 c\ g \frac{\rho}{\mu} \qquad (2)$$

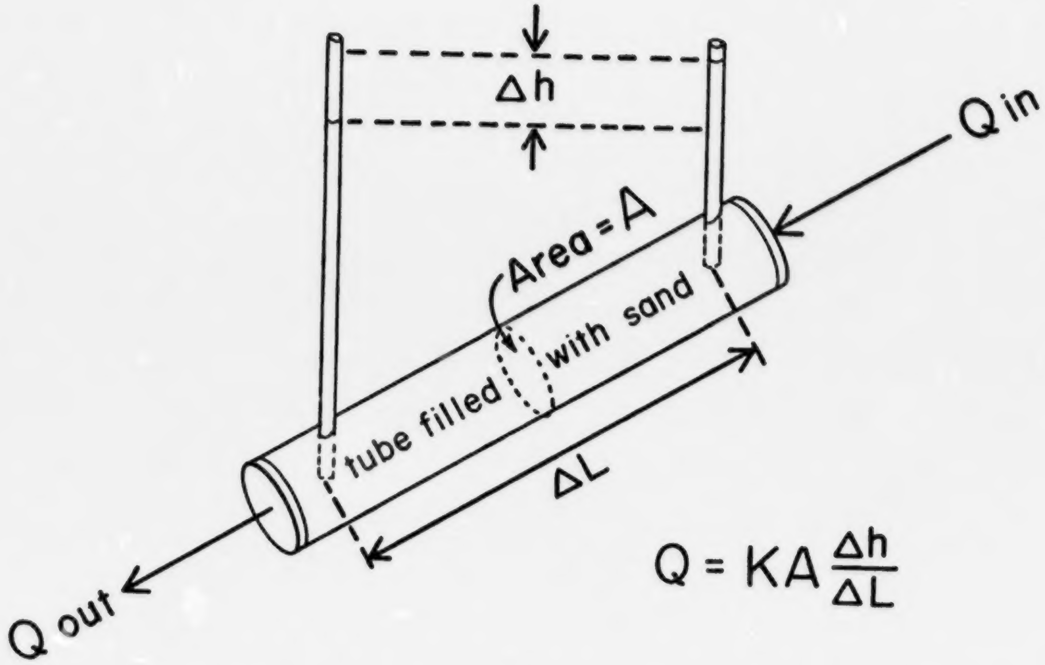


Figure 2.1. An illustration of Darcy's law using a tube filled with sand. The energy loss in the flow system is proportional to the change in hydraulic head, Δh, over an incremental length, ΔL, and inversely proportional to the hydraulic conductivity, K, which is a constant only if the fluid properties and the gravitational field are constant. The discharge, Q, flowing through the tube is measured in any consistent units of volume per unit time ($length^3$/time).

where d is some average aperture width, such as the diameter of pores between sand grains or the width of cracks in rocks; c is a unitless measure of the geometry of the pores; g is the acceleration of gravity; ρ is the density of the fluid; and μ is the dynamic viscosity of the fluid. The product d^2c in Equation (2) is commonly designated as the permeability, k, of the solid material. The older hydrologic and engineering literature commonly uses the term "permeability" to designate hydraulic conductivity. The permeability, however, is a property of the solid material through which the water (or other fluid) is moving. In contrast, the hydraulic conductivity includes the properties of the fluid and the field of gravity as well as the permeability. Typical values for the hydraulic conductivity, K, and the permeability, k, of natural materials are given in Table 2.1.

Another equation expressing the conservation of mass of water, assuming that water is incompressible, is useful in the consideration of tracer movement. This equation in simple form states that:

$$Q = \overline{v}\, n_e A \tag{3}$$

in which Q and A are identical to these terms found in Equation (1), and $\overline{v}$ is the average velocity of the ground water. The term n_e is the effective porosity, or the pore volume which transmits ground water.

In most sections of this manual, it is assumed that porosity, permeability, and hydraulic conductivity are constants in a given field situation. Under most conditions, these values can vary widely in space and will even vary with time. Spatial variations are evident in all geologic materials and need no explanation at this point. Temporal variations are not as

TABLE 2.1

Representative Values of Porosity,
Hydraulic Conductivity, and Permeability
[Data abstracted from several sources including Davis (1969)]

Material	Porosity (%)	Hydraulic Conductivity (meters/day)	Permeability (darcys)
Granite, dense	0.3	1.5×10^{-6}	2.0×10^{-6}
Granite, fractured	1.2	2×10^{-2}	2.7×10^{-2}
Quartzite, dense	0.6	1.4×10^{-6}	1.9×10^{-6}
Schist, highly-weathered, clay-rich	48	2.3×10^{-2}	3.1×10^{-2}
Schist, fractured and partly weathered	5	1.04	1.4
Basalt, dense	7.7	1.04×10^{-5}	1.4×10^{-5}
Tuff, friable	36	1.04×10^{-3}	1.4×10^{-3}
Conglomerate, highly-lithified	17.3	3.6×10^{-4}	4.9×10^{-4}
Sandstone, medium-grained	15.6	5.6×10^{-2}	7.6×10^{-2}
Shale, compacted	21	3×10^{-6}	4×10^{-6}
Limestone, dense	10.1	5.7×10^{-3}	7.7×10^{-3}
Clay, marine	48.5	1.2×10^{-5}	1.6×10^{-5}
Sand, medium-grained	42.9	13.5	18.2
Sand, medium to coarse-grained	37.4	20.4	27.5
Sand, fine-grained	40.1	1.1	1.5
Silt, sandy	39.4	2.8×10^{-2}	3.8×10^{-2}
Silt, loess, fine-grained	50.0	0.24	0.33
Gravel, fine-grained, some sand	32.1	66	89

Note: With water at 20°C, material having one darcy permeability will have a hydraulic conductivity of 0.74 meters/day which is equivalent to 2.43 feet/day.

self-evident; however, they can also be very large. Examples would be the variations caused by the effects of natural or artificial compaction of sediments, the dissolution of minerals making up the solid matrix under consideration, the deposition of mineral matter, and, very importantly, the expansion or contraction of clays and other fine-grained material in response to changes in water chemistry. The last example becomes very important when considering the use of artificially introduced tracers.

Direction of Water Movement

In order to complete a tracer test using more than one well, the general direction of ground-water movement should commonly be known. This is particularly true if the travel of tracers is to be studied using two wells with ground water flowing under a natural gradient. As a first approximation, ground water will flow in the direction of the steepest hydraulic gradient. This direction is generally perpendicular to lines of equal ground-water levels as defined by water levels in wells penetrating the water-bearing zone of interest (Figure 2.2).

Unfortunately, local differences in hydraulic conductivity may amount to several orders of magnitude. Local flow directions may then be highly distorted, and actual directions will diverge widely from directions predicted on the basis of widely spaced water wells (Figure 2.3). It is not at all uncommon to inject a tracer in a well and not be able to intercept that tracer in another well just a few meters away, particularly if the tracer flows under the natural hydraulic gradient which is not disturbed by pumping. This problem will be discussed in more detail later in this manual.

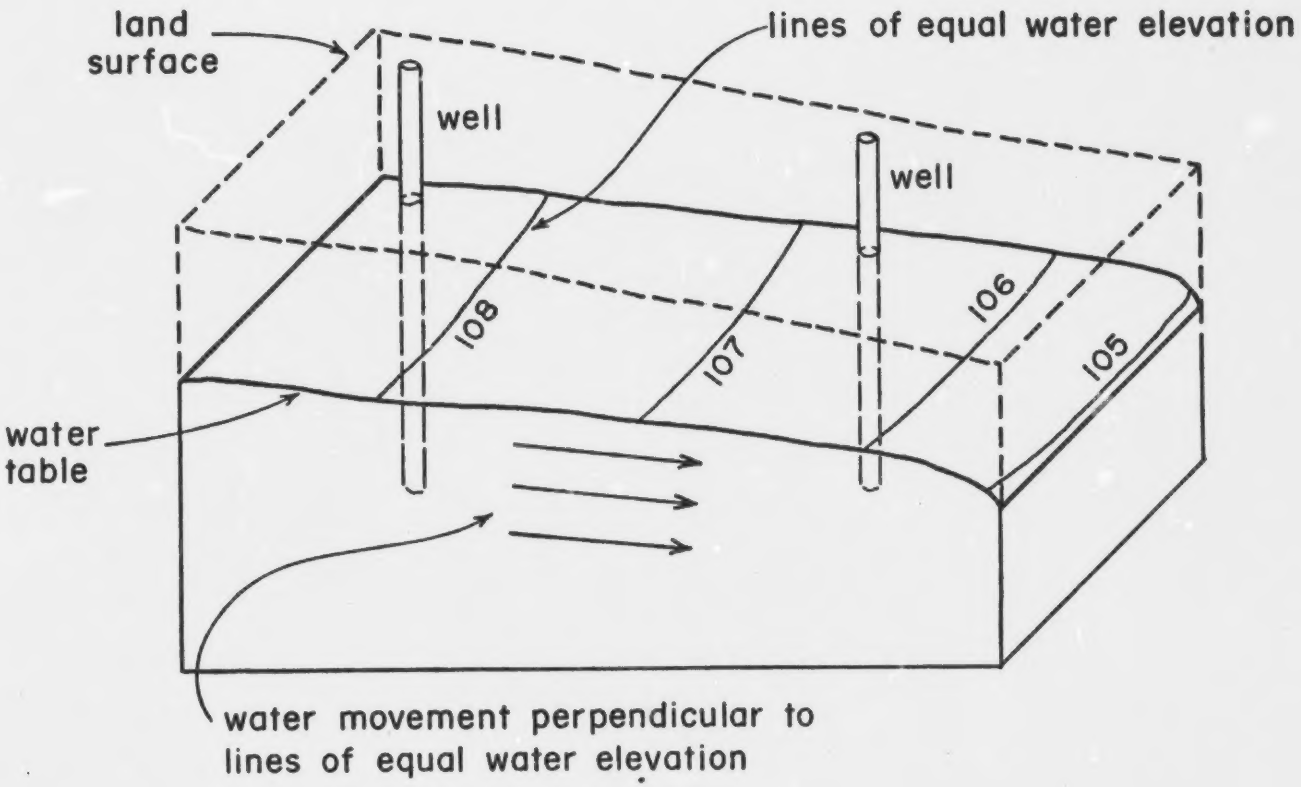

land surface
lines of equal water elevation
well
well
108
107
106
105
water table
water movement perpendicular to lines of equal water elevation

Figure 2.2. Contours of the water table are established by measuring the elevation of water levels in wells. As shown in this figure, ground water will flow in the general direction in which the water level slopes. Unless geologic or hydrologic evidence indicates otherwise, ground water is assumed to flow exactly perpendicular to the lines of equal water elevation.

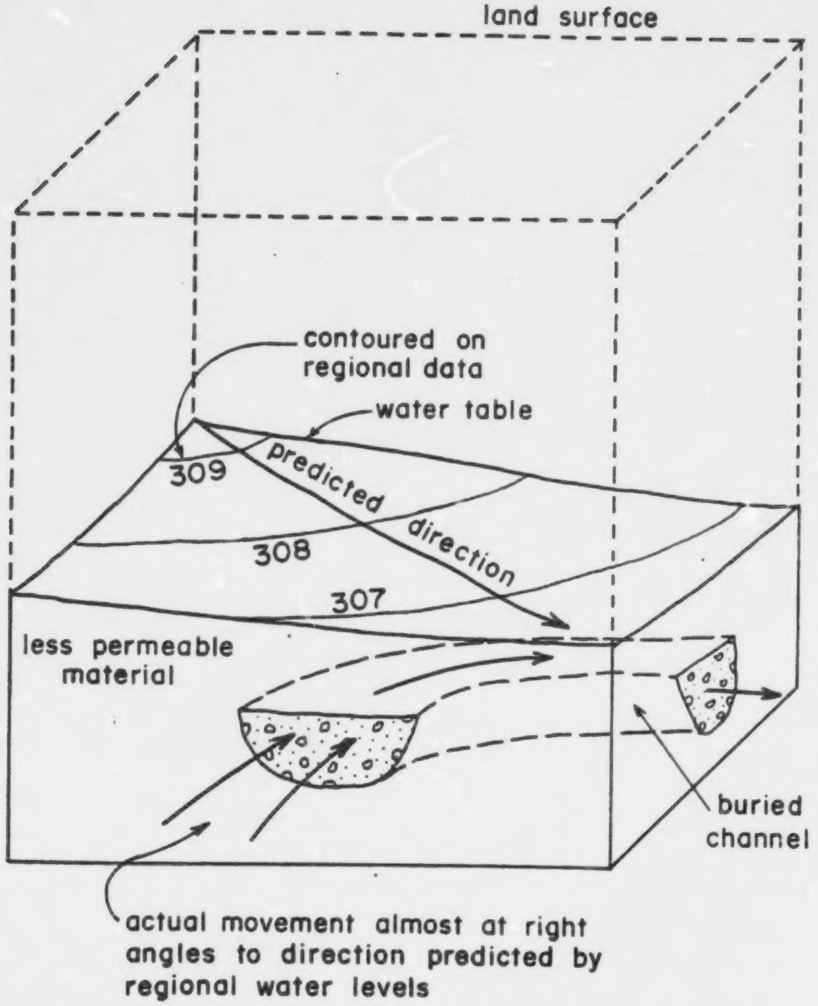

land surface
contoured on
regional data
water table
309
predicted
direction
308
307
less permeable
material
buried
channel
actual movement almost at right
angles to direction predicted by
regional water levels

Figure 2.3. Although regional data from widely separated wells may suggest a certain direction of ground-water flow, local zones of high permeability caused by fractures in rock, solution openings, or local zones of coarse sediments like that shown in this figure may divert the flow in an entirely different direction. This effect is one of the most common causes of failures in ground-water tracing attempts. Tracers injected in one well simply do not travel to the sampling point because of heterogeneities in the system.

Travel Time

The term $\overline{v}$ in Equation (3) can be replaced by $\frac{\Delta L}{\Delta t}$, where Δt is the length of time taken by the average water particle to move through a distance of ΔL. Then Equations (1) and (3) can be combined and the identical term A (area) cancelled, resulting in the equation:

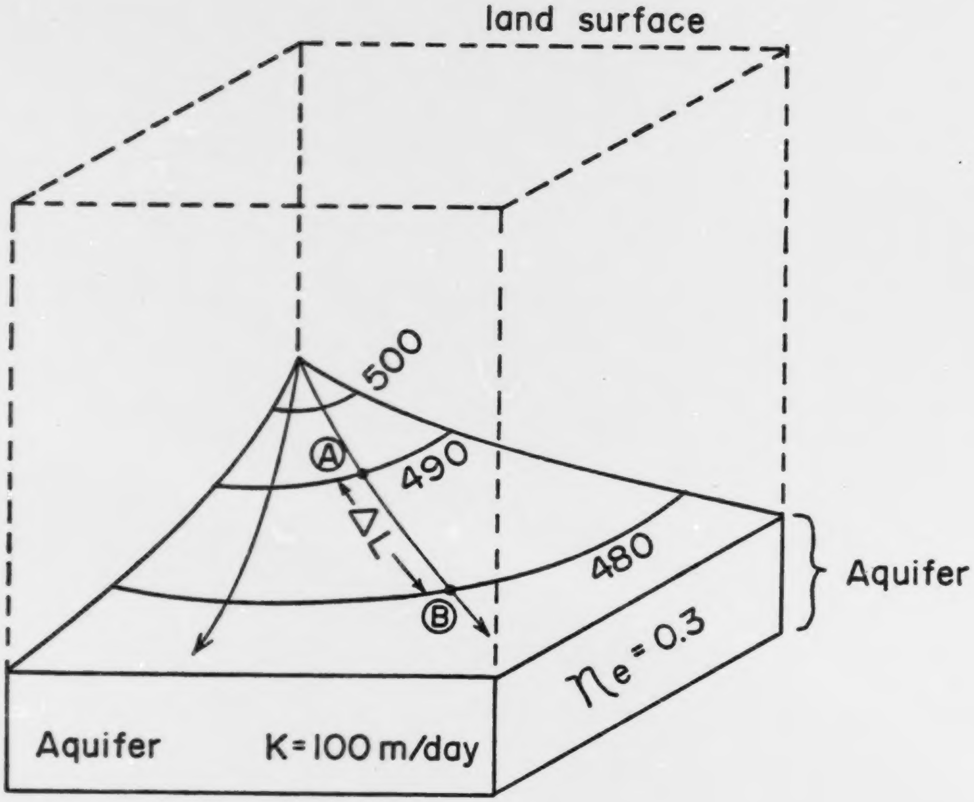
$$t = \frac{ne(\Delta L)^2}{K\Delta h} \tag{4}$$

This equation can be used to estimate the time which would be taken by water to travel from one point to another. If a tracer is injected which travels with the water, t is also the travel time of the tracer. The use of Equation (4) is illustrated in Figure 2.4.

One of the common errors in tracer tests is to conduct tests between points which are separated by too great a distance. As can be seen in Equation (4), the expected travel time for a given head drop is a function of the distance squared (ΔL^2) and therefore increases very rapidly with the distance, ΔL. Thus, a tracer test in one region using a specific hydraulic head drop of Δh over a distance of 1,000 meters would take 10,000 times as long as a test in another region over a distance of 10 meters which has the same head drop, provided the effective porosities and hydraulic conductivities are identical.

Sorption of Tracers and Related Phenomena

Sorption occurs when a dissolved ion or molecule becomes attached to the surface of a solid or dissolves in the solid. Electrostatic, hydrophobic, and chemical forces are involved in sorption. Various types of


land surface
500
490
480
Ⓐ
ΔL
Ⓑ
Aquifer
$n_e = 0.3$
Aquifer
K=100 m/day

If $\Delta L = 1000$ meters

then $$t = \frac{(.3)(1000)^2}{(100)(10)} = 300 \text{ days}$$

Figure 2.4. The average travel time of ground water between two points A and B can be estimated by means of Equation (4) where the gradient, $\Delta h/\Delta L$, the hydraulic conductivity, K, and the porosity, n_e, are known or can be estimated closely. The value of Δh in the illustration is the difference in the hydraulic head between points A and B (490-480 meters).

sorption are due to ion exchange, induced dipole moments, hydrogen bonding, ligand exchange, and chemical bonding. The term "sorption," as used in this manual, includes the sum of these physical-chemical phenomena. Commonly, two different words are used to describe the broad process of sorption. These are adsorption, a strictly surficial phenomenon, and absorption, a phenomenon which involves movement of material from solution to sites within the structure of the solid phase. Most sorption processes which we will consider are relatively fast, reversible reactions; that is, the dissolved constituent which is sorbed from the water can be released to the water again under favorable circumstances. Cation exchange is probably the most familiar type of adsorption, and is a good example of reversible sorption.

Molecules of some tracers have a tendency to be sorbed on the surfaces of solids for brief periods, after which they move off the solid and into the water again. If the water is moving, the tracer molecules move at a slower rate than the water molecules, because tracer molecules spend part of their time sorbed on solids. Thus, the sorptive characteristics of a tracer must be known in order to design meaningful tracer experiments. One equation for the relative average velocities of water, $\overline{v}_w$, and of the sorbed species, $\overline{v}_s$, is:

$$\frac{\overline{v}_s}{\overline{v}_w} = \frac{1}{1 + K_d \frac{\rho_b}{n}} \qquad (5)$$

in which K_d is a distribution coefficient, ρ_b is the bulk dry density, and n is the porosity of the material in question. Values of K_d can range from almost zero cm^3/gram to more than 1,000 cm^3/gram. The higher values of K_d

would mean that the dissolved species is going to be almost stationary in comparison with the water.

The distribution coefficient of a tracer, K_d, is a complex function of a number of variables, including the chemical nature of the tracer, the concentration of the tracer, and the concentrations and chemical characteristics of other dissolved species in the water within which the tracer moves. The K_d value also depends upon the total surface area and the surface chemistry of the solids in contact with the tracer, the solution temperature. It may also be dependent upon the velocity of the water moving past the solid surfaces. Generally speaking, the value of K_d is lowered by increasing the concentrations of dissolved species in the water. Solid materials which tend to sorb material from water will tend to increase the K_d values of aquifer material. Some natural solids with high sorptive capacities are clay minerals, metal oxides, organic particles, certain micas, and natural zeolites.

Certain tracers discussed later in this manual will be virtually unaffected by sorptive processes. Those tracers are commonly called conservative tracers because their concentrations, and hence their direct relation to the moving ground water, will be conserved if hydrodynamic dispersion is not considered.

Although unlikely in most artificially-introduced tracer experiments, the possibility of mineral dissolution or precipitation should always be kept in mind. As a simple example, if the sulfate ion is used as a tracer in water which moves through a natural bed of gypsum, dissolution of the gypsum will undoubtedly add sulfate to the ground water and may confuse the interpretation of the experiment.

Hydrodynamic Dispersion and Molecular Diffusion

Two natural phenomena, hydrodynamic dispersion and molecular diffusion, always work together to dilute the concentrations of artificially-injected tracers. These phenomena are complex and their effects are difficult to separate in field experiments. The two phenomena are, however, theoretically quite distinct. Hydrodynamic dispersion is produced by natural differences in the local ground-water velocities related to the local differences in permeabilities (Figure 2.5). Molecular diffusion is produced by differences in chemical concentrations which tend to be erased in time by the random motion of molecules (Figure 2.6). Generally, short-term tracer experiments in permeable material will be affected almost exclusively by hydrodynamic dispersion. In contrast, the concentrations of natural tracers moving very slowly in highly heterogeneous materials will be affected profoundly by molecular diffusion.

The phenomena of dispersion and diffusion are discussed in greater detail in Appendix B. A qualitative picture of the expected effects of dispersion, diffusion, and sorption in a simple one-dimensional flow system is offered at the end of Chapter 3.

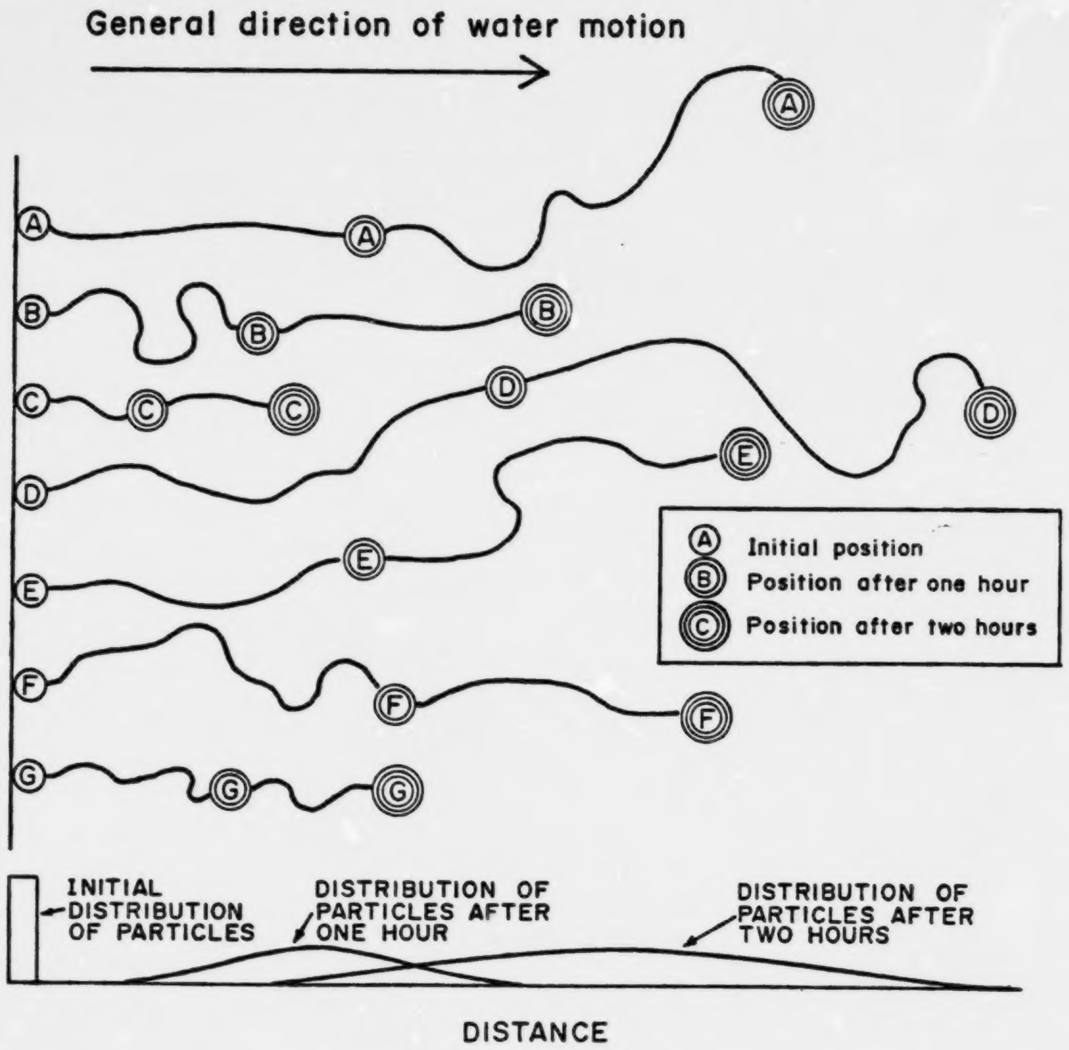

General direction of water motion
A
B
C
D
E
F
G
Ⓐ Initial position
Ⓑ Position after one hour
Ⓒ Position after two hours
INITIAL DISTRIBUTION OF PARTICLES
DISTRIBUTION OF PARTICLES AFTER ONE HOUR
DISTRIBUTION OF PARTICLES AFTER TWO HOURS
DISTANCE

Figure 2.5. Hydrodynamic dispersion is caused by unequal velocities of the ground water. In this figure, a few molecules of a tracer are assumed to have been released at the same time and subsequently carried by the ground water towards the right side of the diagram. The bottom graph shows the general distribution of molecules after one hour and after two hours. Only longitudinal dispersion is shown on this two-dimensional diagram.

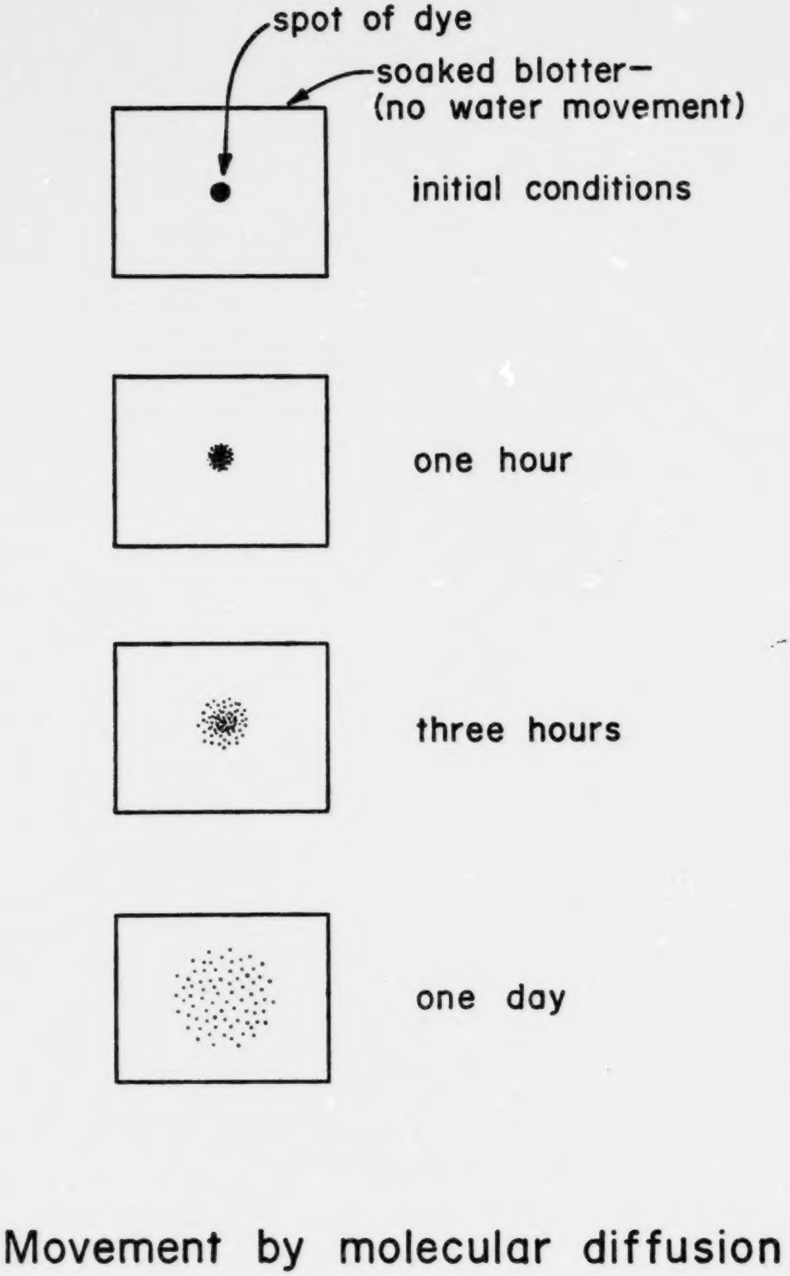

spot of dye
soaked blotter—
(no water movement)
initial conditions
one hour
three hours
one day
Movement by molecular diffusion

Figure 2.6. The movement of dissolved material by molecular diffusion can be seen in a blotter saturated with water. A small dot of dye will move radially outward in the saturated blotter. If the blotter is horizontal, the radial movement of the dye is by molecular diffusion.

CHAPTER THREE

PRACTICAL ASPECTS

Planning a Test

The purpose and practical constraints of a potential tracer test must be understood clearly prior to actual planning of tracer tests (see Appendix C). Is only the direction of water flow to be determined, or are other parameters such as travel time, porosity, and hydraulic conductivity of interest? How much time is available for the test? If answers must be obtained within a few weeks, then tracer tests using only the natural hydraulic gradient between two wells which are more than about 20 meters apart would normally be out of the question because of the long time period needed for the tracer to flow between the wells. Another primary consideration is the budget. If several deep holes are to be drilled, if packers are to be set to control sampling or injection, and if hundreds of samples must be analyzed in an EPA certified laboratory, then total costs could easily exceed a million dollars. In contrast, some short-term tracer tests may be possible at costs of less than a thousand dollars.

The initial step in determining the physical feasibility of a tracer test is to collect as much hydrogeologic information as possible concerning the field area. The logs of the wells at the site to be tested, or logs of the wells closest to the proposed site, should be obtained. Logs will give some idea of the homogeneity of the aquifer, layers present, fracture patterns, porosity, and boundaries of the flow system. Local or regional piezometric maps, or any published reports on the hydrology of the area (including results of aquifer tests) are valuable, as they may give an indication of the hydraulic gradient and hydraulic conductivity.

The hydrogeologic information is used to estimate the direction and magnitude of the ground-water velocity in the vicinity of the study area (Fetter, 1981). One method to arrive at a local velocity estimate is the use of water-level maps together with Darcy's Law, if transmissivity, aquifer thickness, and head values are available (see Chapter Two). The second method involves using a central well with satellite boreholes, and running a preliminary tracer test. The classical method for determining the regional flow direction is to drill three boreholes at extremities of a triangle, with the sides 100-200 meters apart (Figure 3.1). The water levels are measured and the line of highest slope gives the direction of flow. However, regional flow is generally not as important as local flow in most tracer tests, and the importance of having an accurate flow direction cannot be overemphasized. Gaspar and Oncescu (1972) described a method to determine local flow direction by drilling 5-6 satellite wells in the general direction of flow. They noted that the satellite boreholes should be at a minimum distance of 8x the well diameter from the injection well. The boreholes should be screened and gravel packed to avoid well-bore effects. Commonly, the boreholes are 2-3 meters from the central well. The advantage of knowing the general flow direction is that fewer observation wells will eventually be drilled. If a preliminary value of the magnitude of the natural velocity of the aquifer is available, then the injection or pumping rate necessary to obtain radial flow can be determined. Also, when a velocity magnitude is obtained from the preliminary test or available data, a decision as to the distance from the injection well to observation well(s) can be made. This decision depends on whether the test is a natural flow or induced flow (injection or pumping) type test. Natural flow tests are less common due to the greater amount of time involved.

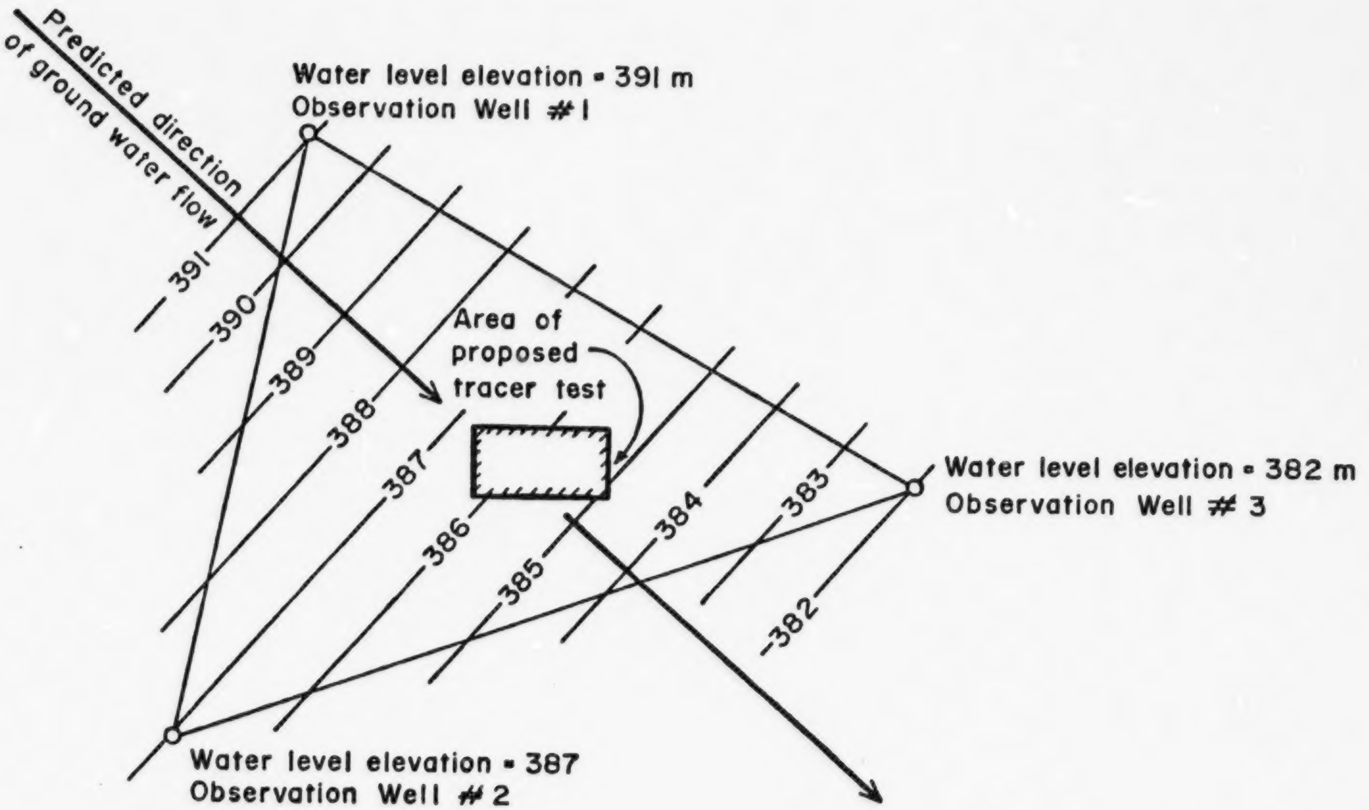

Predicted direction of ground water flow
Water level elevation = 391 m
Observation Well #1
391
390
389
388
387
386
385
384
383
382
Area of proposed tracer test
Water level elevation = 382 m
Observation Well # 3
Water level elevation = 387
Observation Well #2

Figure 3.1. For tests using artificially-injected tracers which will flow by a natural ground-water gradient from one well to another, it is essential to know the direction of ground-water flow prior to the final design of the tests. One method to estimate this direction is to construct a local water-level map near the site of the test and assume that the flow is going to be perpendicular to the lines of equal water elevation. The minimum number of wells needed for the water-level map is three, as shown in this hypothetical example.

A second major consideration when planning a test is which tracers are the best for the conditions at the site and the objectives of the test. Samples of well water should be analyzed for background values of relevant parameters, such as temperature, major ions, natural fluorescence, fluorocarbons, etc. Choice of a tracer will depend partially on which analytical techniques are easily available (see Appendix E) and which background constituents might interfere with these analyses. Various analytical techniques incorporate different interferences, and consultation with the chemist or technician who will analyze the samples is necessary.

Determination of the amount of tracer to inject is based on the natural background concentrations detection limit for the tracer, and the dilution expected (Figure 3.2). If a value for porosity can be estimated, the volume of voids in the medium can be calculated as the volume of a cylinder with one well at the center and the other a distance away. Adsorption, ion exchange, and dispersion will decrease the amount of tracer arriving at the observation well, but recovery is usually not less than 20% (of the injected mass) for two-hole tests using a forced recirculation system and conservative tracers. The concentration should not be increased so much that density effects become a problem. Lenda and Zuber (1970) gave graphs which can be used to estimate the approximate quantity of tracer needed. The values are based on estimates of the porosity and dispersion coefficient of the aquifer.

Types of Tracer Tests

The variety of tracer tests is almost infinite when one considers the various combinations of tracer types, local hydrologic conditions, injection methods, sampling methods, and the geological setting of the site (Appendix

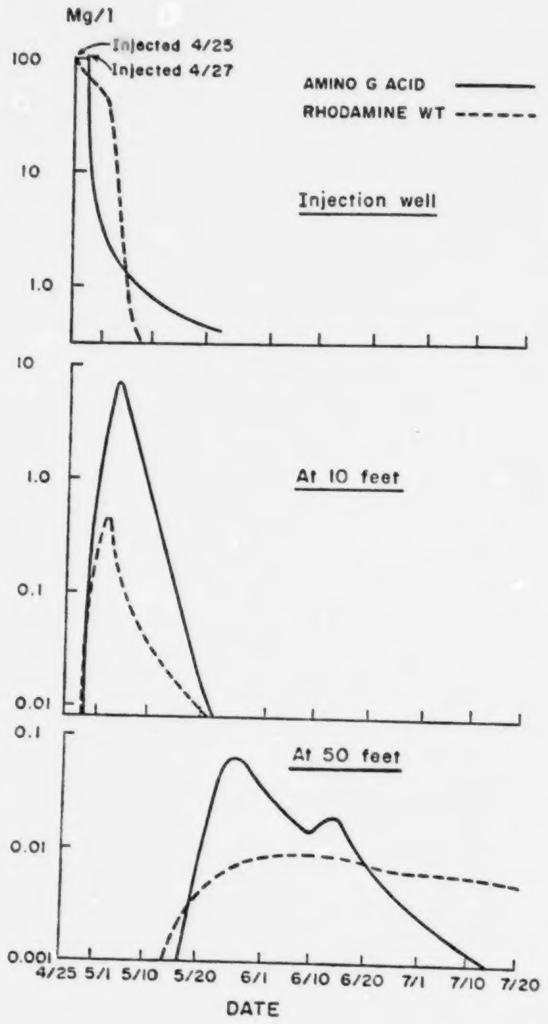


Figure 3.2. Results of tracer tests at the Sand Ridge State Forest, Illinois. The aquifer was a fine to medium coarse dune sand in the upper part and a medium to coarse sand in the lower part. Three injection wells 3 ft apart were used to make 3 separate injections of Lissamine FF (green dye), Amino G Acid (blue, optical brightener), and Rhodamine WT (orange dye). A slug having a uniform concentration of 100 mg/l was used. Lissamine was not detected in any of the observation wells during the duration of the test. Dilution in the injection wells and movement of the dye was entirely by ground water flowing under a natural gradient of 1.5×10^{-3}. Variations of shapes of breakthrough curves are caused by heterogeneities in the aquifer. Note the ten-thousand fold decrease of concentration of Rhodamine produced by only 50 ft of flow. (Data from Naymik and Sievers, 1983).

C). Some of these varieties are shown in Figure 3.3. The following sections discuss a few of the more common types of tracer tests.

Differences in the tests are due to the parameters (such as velocity, dispersion coefficient, and porosity) which are to be determined, the scale of the test, and by the number of wells to be used.

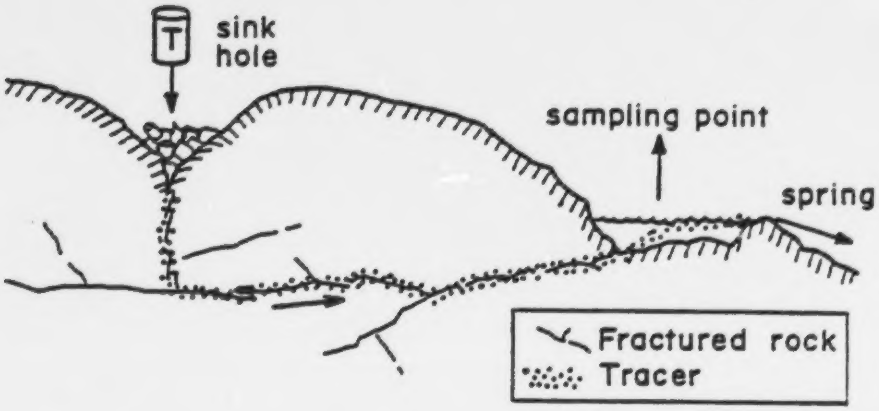
Single-Well Techniques

Two techniques, injection/withdrawal and point dilution, give values of parameters which are valid at a local scale. Advantages of single-well techniques are: (1) less tracer is required than for two-well tests; (2) the assumption of radial flow is generally valid so natural aquifer velocity can be ignored, making solutions easier; and (3) knowledge of the exact direction of flow is not necessary.

Injection/Withdrawal

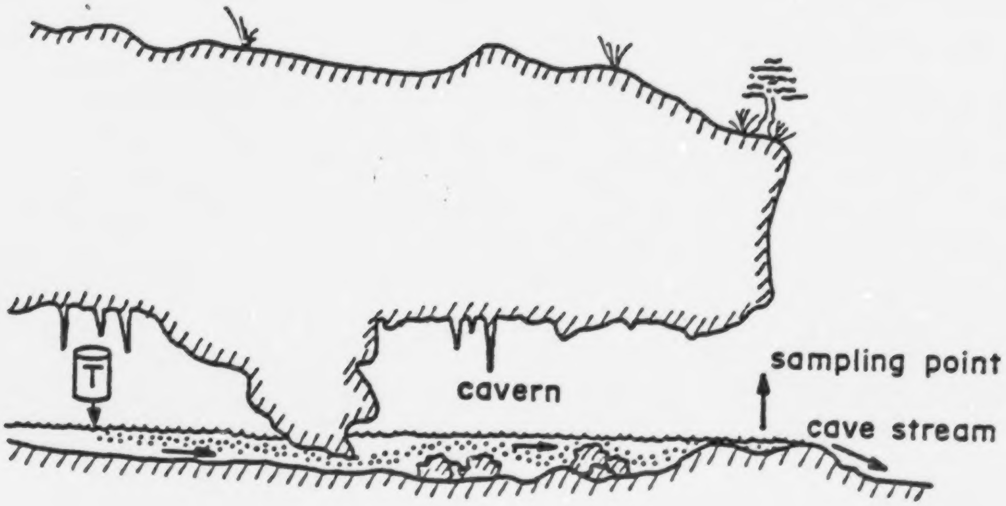
The single-well injection/withdrawal (or pulse) technique results in a value of pore velocity and the longitudinal dispersion coefficient. The method assumes that porosity is known or can be estimated with reasonable accuracy. A given quantity of tracer is instantaneously added to the borehole, the tracer is mixed, and then 2-3 borehole volumes of fresh water are pumped in to force the tracer to penetrate the aquifer. Only a small quantity is injected so that natural flow is not disturbed. After a certain time, t, the tracer has traveled a distance X, due to uniform flow. Then the borehole is pumped out at a constant rate which is large enough to overcome uniform flow. Tracer concentration is measured with time or pumped volume. This enables one to find the distance traveled, X, by the relationship:

Figure 3.3. A number of common configurations for ground-water tracing by the use of artificially-injected tracers are shown in the following diagrams. Although single tracers are shown in most of the diagrams, most tests can use more than one tracer. Also, the purposes are varied and only the most obvious ones are mentioned. Sampling of the initial mixture of the tracer and water prior to injection is not shown but is almost always required if quantitative results are to be obtained.


T
sink hole
sampling point
spring
Fractured rock
Tracer

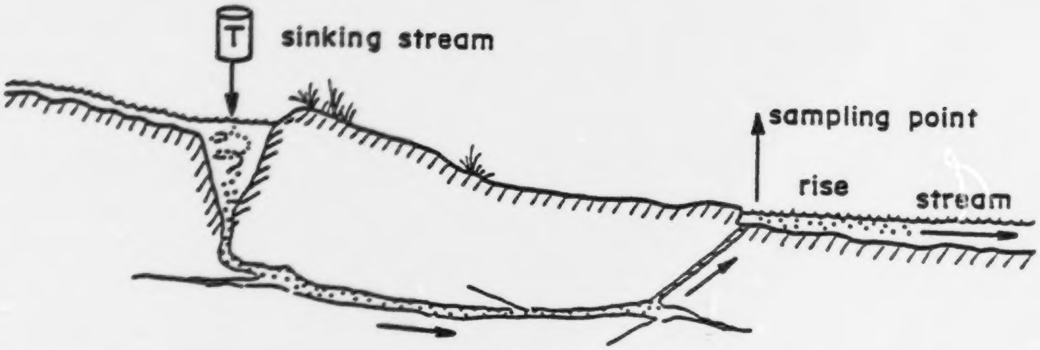
(a.)

Determine if trash in sinkhole contributes to contamination of spring.


T
cavern
sampling point
cave stream

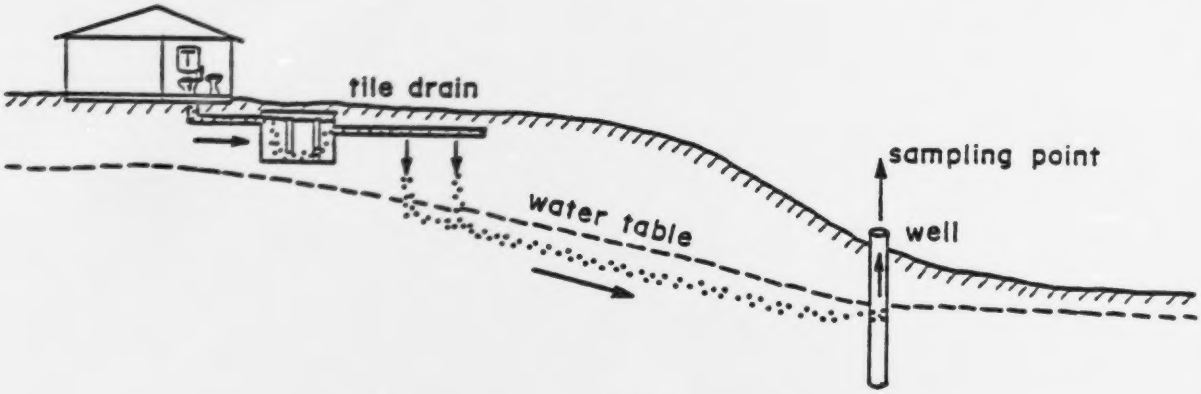
(b.)

Measure velocity of water in cave stream.


T
sinking stream
sampling point
rise
stream

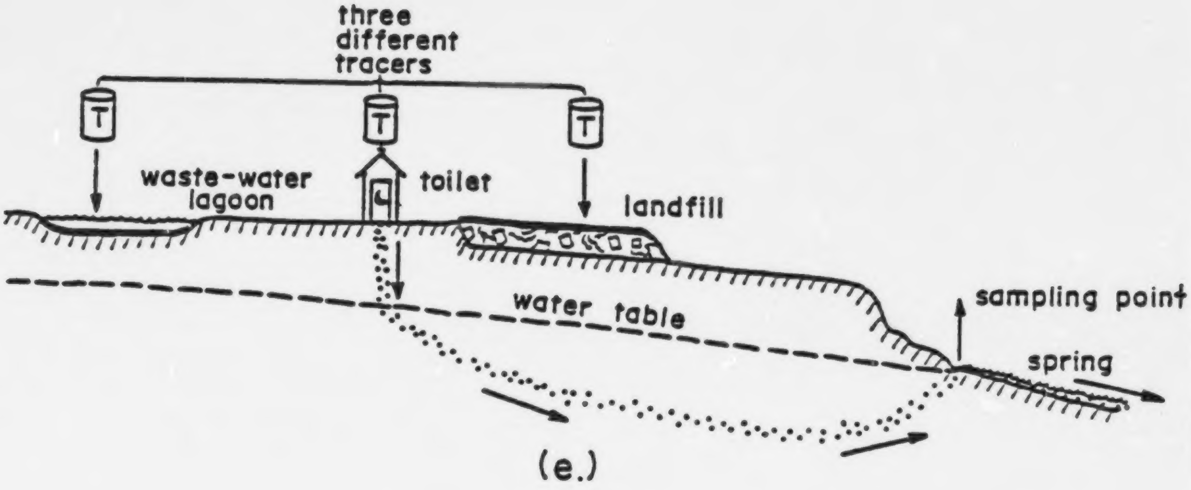
(c.)

Check source of water at rise in stream bed.

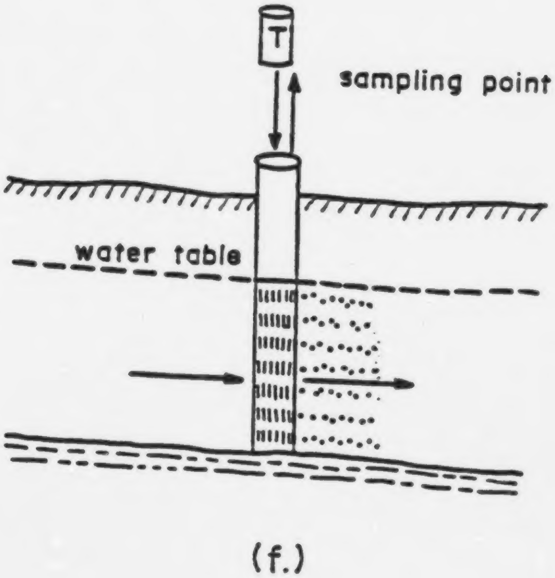

T
tile drain
sampling point
water table
well

(d.)

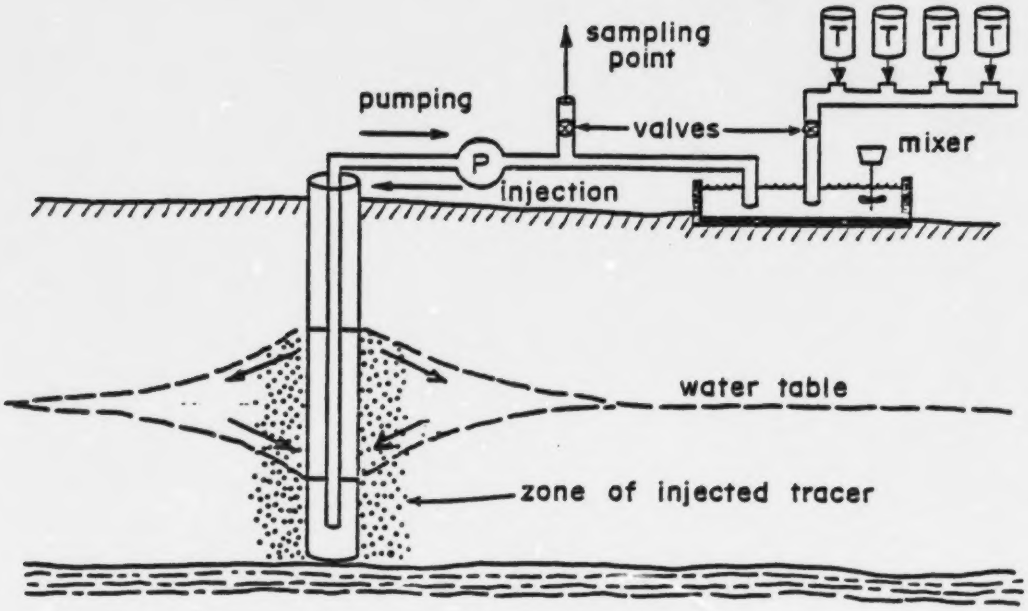
Determine if tile drain from septic tank contributes to contamination of well.


three different tracers
T
T
T
waste-water lagoon
toilet
landfill
water table
sampling point
spring
(e.)

Determine source of pollution from three possibilities.

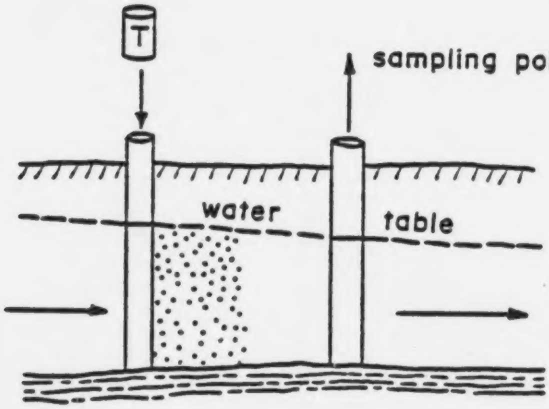

T
sampling point
water table
(f.)

Determine velocity and direction of ground-water flow under natural conditions. Injection followed by sampling from same well.


sampling point
T
T
T
T
pumping
valves
mixer
P
injection
water table
zone of injected tracer

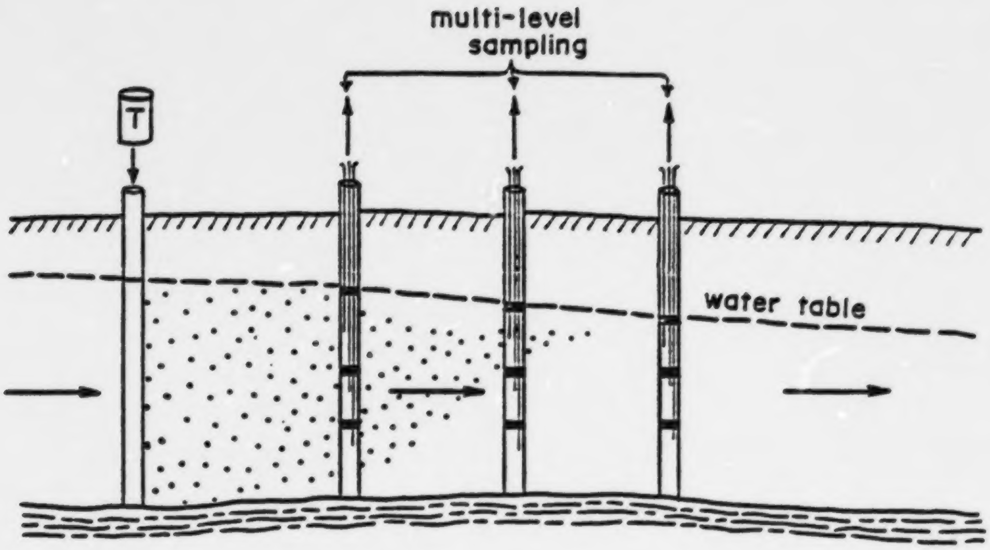
(g.)

Test precipitation of selected constituents on the aquifer material by injecting multiple tracers into aquifer then pumping back the injected water.


T
sampling point
water
table

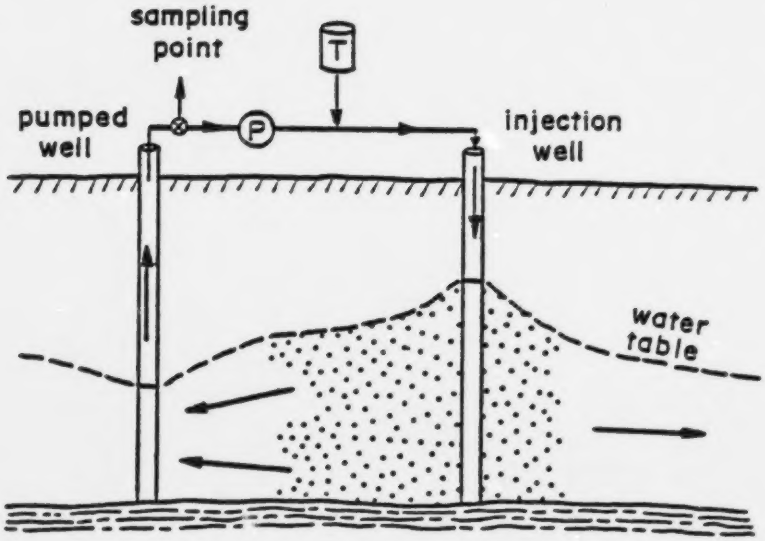
(h.)

Test velocity of movement of dissolved material under natural ground-water gradients.


multi-level sampling
T
water table

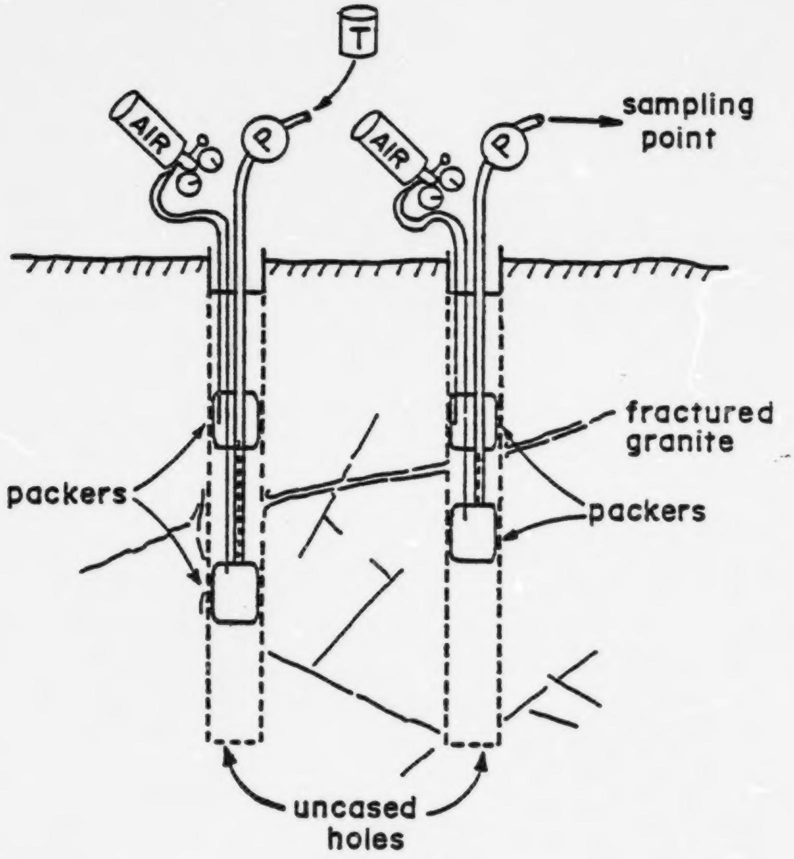
(i.)

Test hydrodynamic dispersion in aquifer under natural ground-water gradients.


sampling point
T
pumped well
P
injection well
water table

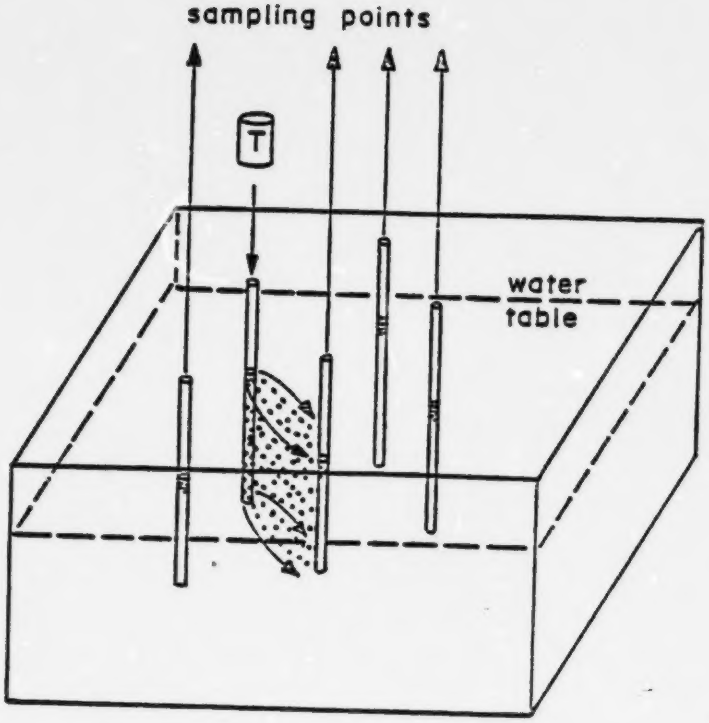
(j.)

Test a number of aquifer parameters using a pair of wells with forced circulation between wells.


T
AIR
P
AIR
P
sampling point
fractured granite
packers
packers
uncased holes

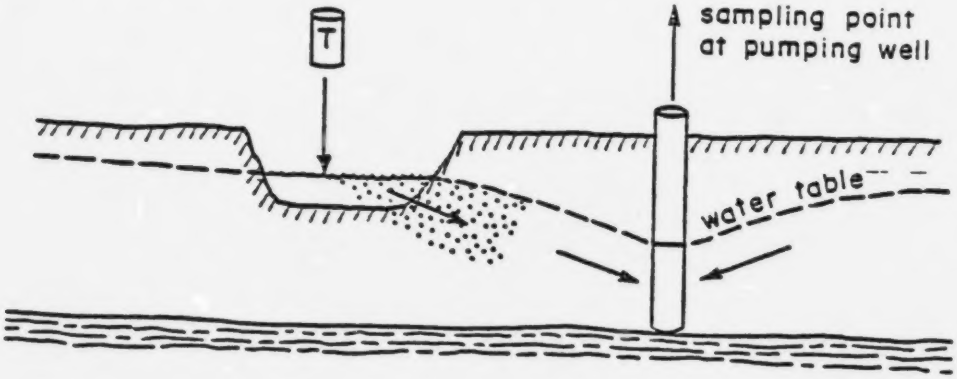
(k.)

Determine the interconnect fractures between two uncased holes. Packers are inflated with air and can be positioned as desired in the holes.


sampling points
T
water table

(l.)

Determine the direction and velocity of natural ground-water flow by drilling an array of sampling wells around a tracer injection well.


T
sampling point at pumping well
water table

(m.)

Verify connection between surface water and well.

$$x = \frac{V\ 50\%}{\pi\ b\ n}$$

where V = volume pumped to recover 50% of the mass injected;

b = aquifer thickness; and

n = porosity.

Average velocity is then $\frac{X}{t}$, where t is time from initial injection to the time when pumping started. If concentration is measured at various depths with point samplers, relative permeability of layers can be determined. The dispersion coefficient is obtained by matching experimental breakthrough curves with theoretical curves based on the general dispersion equation. A finite difference method is used to simulate the theoretical curves (Fried, 1975). Some assumptions of the theory are homogeneous, horizontal, and independent strata. Fried concluded that the method is useful for local information (2-4 meters) and for detecting the most permeable strata. An advantage of this test is that nearly all of the tracer is removed from the aquifer at the end of the test.

Borehole Dilution

Borehole dilution techniques are also described in Chapter Four under radioactive tracers. This technique can be used to measure the magnitude and direction of horizontal tracer velocity (Darcian velocity as described in Chapter Two, not pore velocity) and vertical flow. Also, hydraulic conductivity values can be obtained by applying Darcy's law.

The procedure is to introduce a known quantity of tracer instantaneously into the borehole, mix it well, and then to measure the concentration decrease with time. The equation used to determine velocity is

$$V = \frac{r \ln (C_0/c)}{4\ tn}$$

where r = borehole radius;

t = time of observation; and

n = effective porosity.

Often a correction term for distortion of flow due to the borehole is added. The tracer is generally introduced into an isolated volume of the borehole using packers. Radioactive tracers have been used frequently for borehole dilution tests, but other tracers can be used.

The lower limit of the aquifer velocity for use of this method is $V = 0.01$ m/α, due to diffusion. The upper limit is a few hundred meters per day because flow is no longer laminar. Other assumptions related to this technique are:

(1) Borehole dimensions are well known.

(2) Measurements are taken after steady flow has been established (well screen does not alter flow).

(3) If possible, borehole construction should be such that vertical flow is not present.

(4) If the borehole is screened, the gravel pack should be homogeneous with respect to permeability. Also, the screen and gravel pack should be arranged concentrically within the borehole.

Other factors to keep in mind when conducting a point dilution test are the homogeneity of the aquifer, effects of drilling (mudcake, etc.), homogeneity of the mixture of the tracer and the well water, degree of tracer diffusion, and density effects. A number of corrections are available to correct for well construction, vertical currents, and other factors (Gaspar and Oncescu, 1972).

The ideal condition for conducting the test is to use a borehole with no screen or gravel pack. If a screen is used, it should be next to the borehole as dead space alters the results. Samples should be very small in volume so that flow is not disturbed by its removal.

The time versus concentration curve will be linear in a middle section of the plot. Velocity determinations are reasonably accurate if the linear region is in the area of $c/c_0 < 0.50$. For more information on this type of test, see Gaspar and Oncescu (1972), Fried (1975), and Klotz et al. (1978).

The direction of ground-water flow can be measured in a single borehole by a method similar to point dilution. A tracer (often radioactive) is introduced slowly and without mixing. A section of the borehole is usually isolated by packers. After some time, a compartmental sampler (4-8 compartments) within the borehole is opened. The direction of minimum concentration corresponds to the flow direction. Another similar method is introduction of a radioactive tracer and subsequent measurement of its adsorption on the borehole or well screen walls by means of a counting device in the hole. The method is described in more detail in Gaspar and Oncescu (1972).

Two-Well Techniques

These methods consist of two types, uniform (natural) flow and radial flow tests. The parameters measured (dispersion coefficient and porosity) are assumed to be the same for both types of flow.

Uniform Flow

A tracer is placed in one well without disturbing the flow field and a signal is measured at observation wells. This test can be used at a local (2-5 m) or intermediate (5-100 m) scale, but the time involved in the test is much larger than that related to radial tests. The direction and magnitude of the velocity must be known quite precisely, or a large number of observation wells are needed. The quantity of tracer needed to cover a large distance can be expensive. On a regional scale, environmental tracers are generally used, including seawater intrusion, radionuclides, or stable isotopes of hydrogen and oxygen. Man-made pollution has also been used. For regional problems, a mathematical model is calibrated with concentration versus time curves from field data, and the same model is used to predict future concentration distributions.

Analysis of local or intermediate scale uniform flow problems can be done analytically, semi-analytically, or by curve-matching. Layers of different permeability can cause distorted breakthrough curves, which can usually be analyzed (Gaspar and Oncescu, 1972). One- or two-dimensional models are available. Analytical solutions can be found in Fried (1975) and Lenda and Zuber (1970).

Radial Flow

These techniques are based on imposing a velocity on the aquifer, and generally solutions are easier if radial flow is much greater than uniform flow. A value for natural ground-water velocity is not obtained, but porosity and the dispersion coefficient are.

A diverging test involves constant injection of water into an aquifer with a slug or continuous flow of tracer introduced instantaneously into the injected water. The tracer is detected at an observation well which is not pumping. Very small samples are taken at the observation well so that flow is not disturbed. Packers can be used in the injection well to isolate an interval. Sampling can be done with point samplers or an integrated sample can be taken.

Converging tests involve introduction of the tracer at an observation well and another well is pumped. Concentrations are monitored at the pumped well. The tracer is often injected between two packers or below one packer, and then 2 to 3 well bore volumes are injected to push the tracer out into the aquifer. At the pumping well, intervals of interest are isolated (particularly in fractured rock), or an integrated sample is obtained.

A recirculating test is similar to a converging test, but the pumped water is injected back into the injection well. This tests a significantly greater part of the formation because the wells inject to and pump from 360 degrees. The flow lines are longer, partially canceling out the advantage of a higher gradient. Theoretical curves are available for recirculating tests (see Sauty, 1980).

Design and Construction of Test Wells

In many tracer tests, the construction of test wells is the single most expensive part of the work. It also can be the source of major difficulty if the construction is not done properly. Several texts cover the general details of drilling technology and well construction (California Department of Water Resources, 1968; Campbell and Lehr, 1973; Johnson Division, UOP, Inc., 1972; Todd, 1980) and therefore they are not discussed in this manual.

There are five common types of problems which are encountered with tracer tests. The first problem relates to site selection. If heavy equipment is to be moved into an area, lack of overhead clearance, narrow roads, poor bearing capacities of bridges, and the lack of flat ground at the site can all be major problems. Also, overhead electrical power lines at the site should be avoided. One of the most common hazards is accidental grounding of power lines by drill rigs and auger stems with subsequent electrocution of workers.

The second problem relates to the improper choice of drilling equipment. For some purposes, cheap systems using hand augers and drive points are suitable to install wells for shallow tracer tests (Figure 3.4). To be sure, a large drilling rig could be moved into the site to do the same job, but with at least a ten-fold increase in cost which would be a major misuse of funds. The error is commonly the other direction, however, with attempts to hold down the cost resulting in the use of drilling equipment which is unable to handle the needs of the project. Another general problem relating to drilling is the use of drilling fluids which will affect the tracer tests. Certain drilling muds and mud additives have a very high capacity for the sorption of most types of tracers. The muds could also clog small pores and alter the permeability of the aquifer near the drill hole. The use of compressed air for drilling may avoid some of these problems but it could introduce atmospheric fluorocarbons which could interfere with tracer tests using fluorocarbons.

A third problem is the choice of casing diameter. Ideally, packers should be used to isolate the zones being sampled from the rest of the water in the well (Figure 3.5). For a number of reasons which include economics, insufficient time, and lack of technical training, packers are often not used in tracer tests. In this case, the diameter of the sampling well should be as small as possible in order to minimize the amount of "dead" water in the well during sampling. The diameter, however, cannot be too small because the well must be adequately cleaned after installation and the well must accommodate bailers, pumps, or other sampling equipment. Common casing diameters

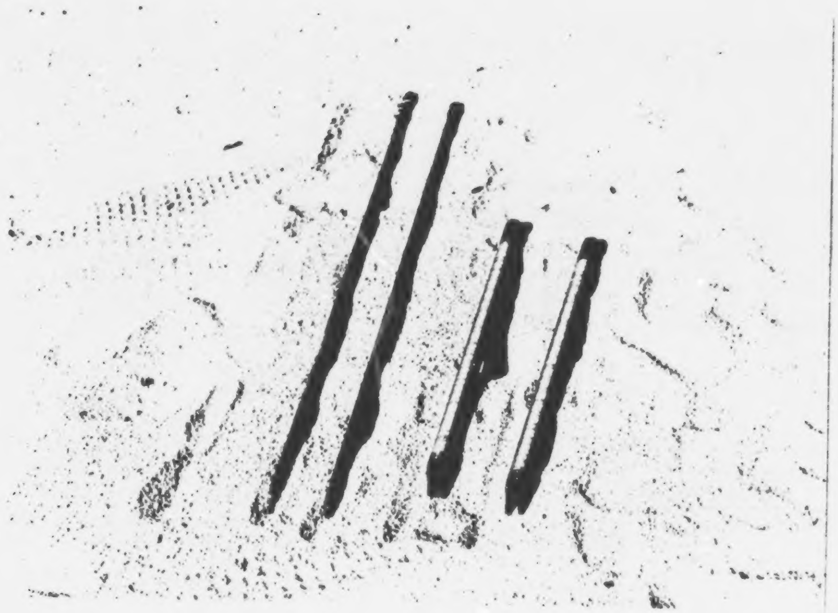


Figure 3.4a. Well installation for a simple tracer test. Two home-made drive points of iron pipe crimped at the ends and perforated by drilled holes are on the left and two standard wire-wound commercially available drive points are on the right. Extension pipe is screwed onto the ends of the drive points in order to reach desired depths. Unless special jetting equipment is used, drive points can usually penetrate only 20 to 30 feet of alluvium.

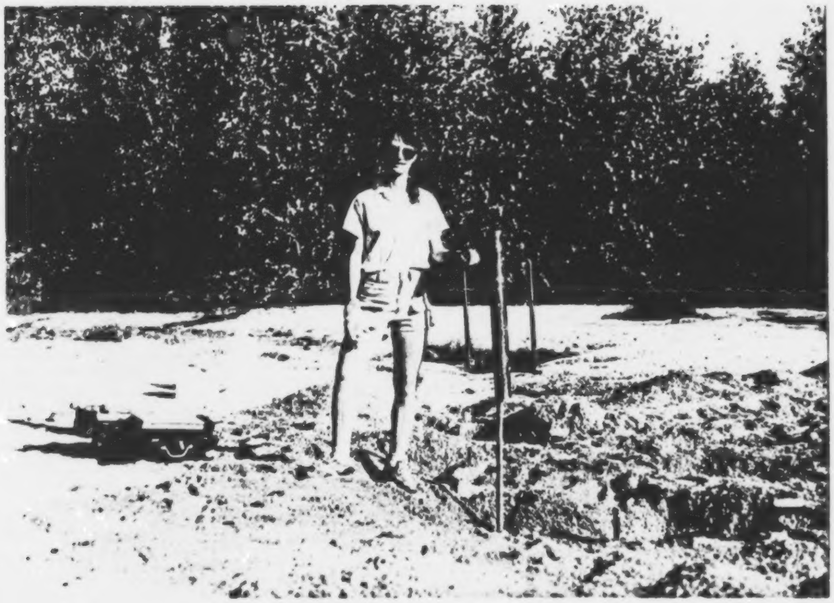


Figure 3.4b. Hammer used to install drive points. The hammer which is shown in this picture is a hollow weighted tube with one closed end and side handles. If alluvium has coarse gravel or cobbles, home-made drive points will collapse easily.

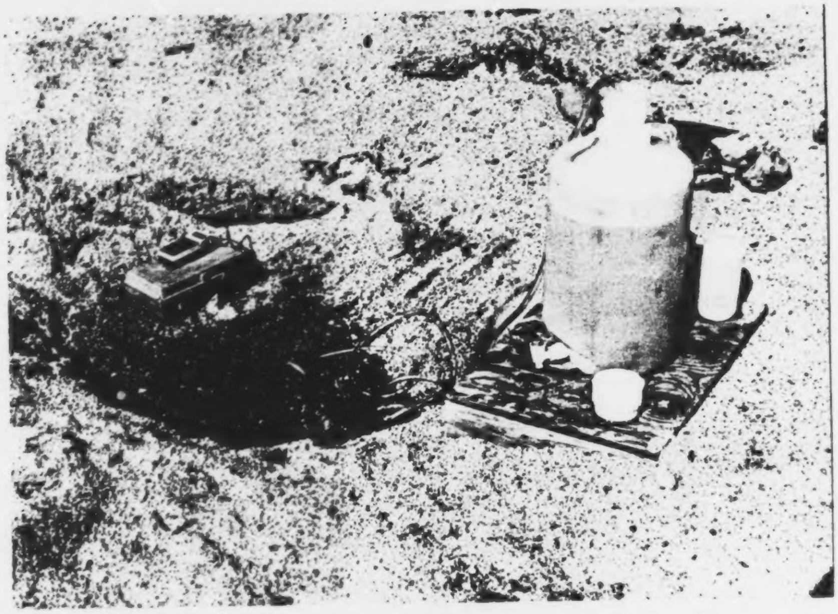


Figure 3.4c. Tracer water being injected into a shallow test hole. Instrument is a thermistor thermometer.

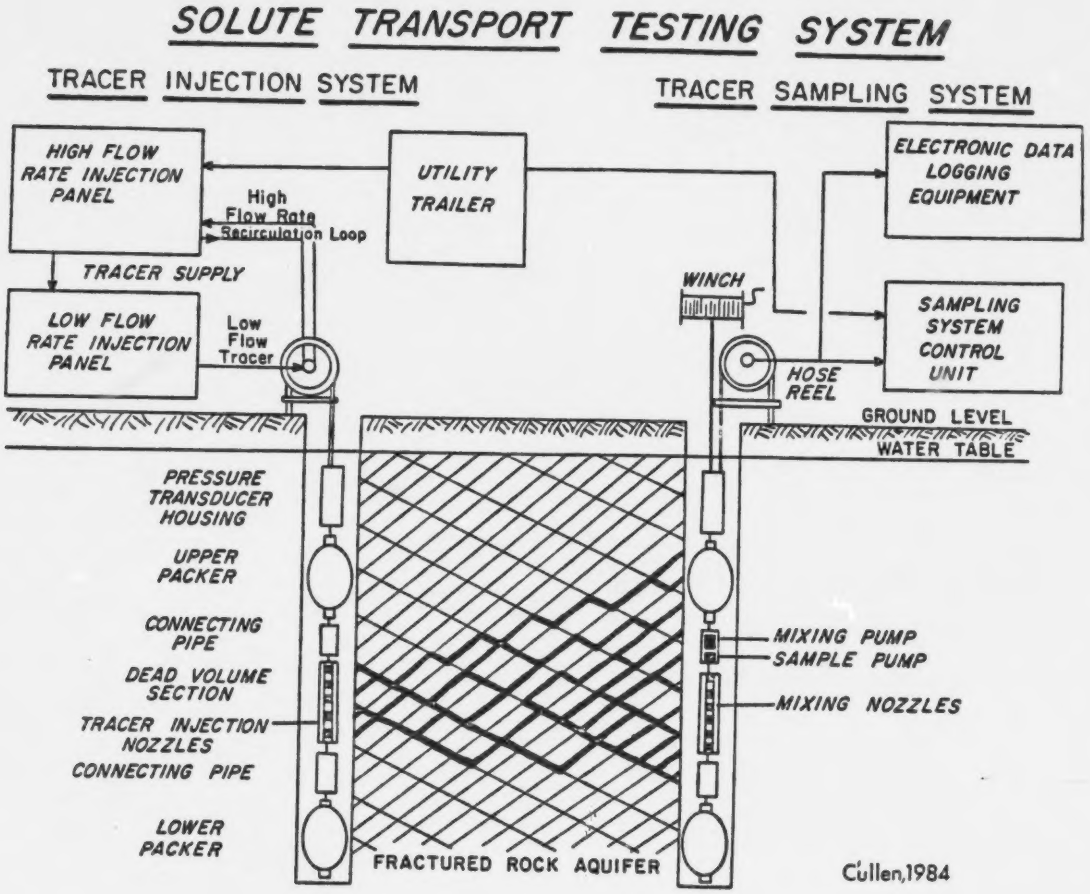

SOLUTE TRANSPORT TESTING SYSTEM
TRACER INJECTION SYSTEM
TRACER SAMPLING SYSTEM
HIGH FLOW RATE INJECTION PANEL
UTILITY TRAILER
ELECTRONIC DATA LOGGING EQUIPMENT
High Flow Rate Recirculation Loop
TRACER SUPPLY
WINCH
LOW FLOW RATE INJECTION PANEL
Low Flow Tracer
SAMPLING SYSTEM CONTROL UNIT
HOSE REEL
GROUND LEVEL
WATER TABLE
PRESSURE TRANSDUCER HOUSING
UPPER PACKER
CONNECTING PIPE
DEAD VOLUME SECTION
TRACER INJECTION NOZZLES
CONNECTING PIPE
LOWER PACKER
MIXING PUMP
SAMPLE PUMP
MIXING NOZZLES
FRACTURED ROCK AQUIFER
Cullen,1984

Figure 3.5. (a) Schematic diagram for a two-well tracer test in fractured rock completed at Oracle, Arizona, by the Department of Hydrology and Water Resources, University of Arizona. The following photograph shows the control panel for the high-flow rate injection with storage tanks for four different tracers arranged on top of the panel box. This is an example of a tracer test which is more complex than commonly attempted for practical applications. Diagram, courtesy of James Cullen.

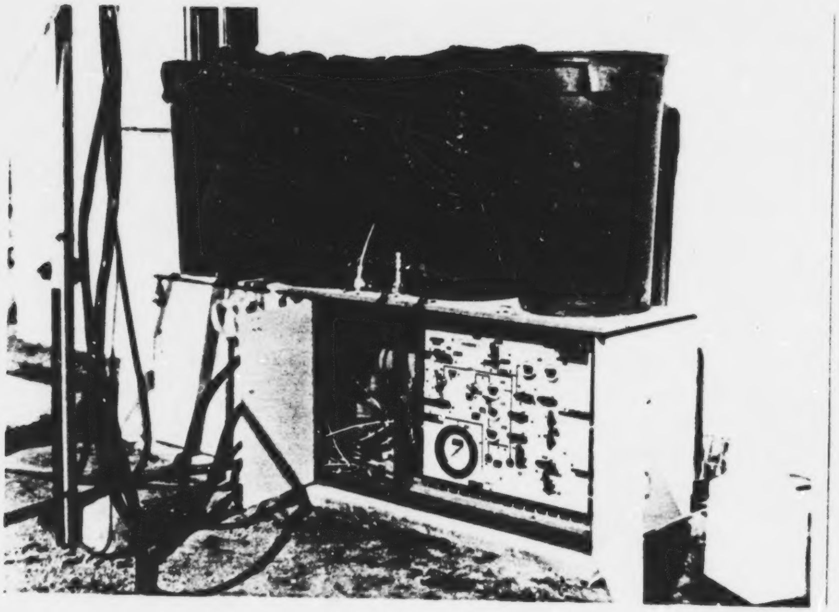


Figure 3.5. (b) High flow rate injection panel shown in diagram in Figure 3.5a.

used range from about 1" to 4" for relatively shallow test holes to as much as 6" to 8" for very deep tests.

The type of casing to be used is a fourth concern primarily if low-level concentrations of tracers are to be used, and in particular if these tracers are organic compounds or metallic cations. For plastic casings, TEFLON absorbs and releases less organics than does PVC. Adhesives used to connect sections of plastic pipes may be also a troublesome source of interferring organic compounds. Metal casing could release trace metals but it is generally superior to plastic casing in terms of strength and sorptive characteristics. Inexpensive metal casing, however, will have a short life if ground waters are corrosive.

A fifth problem is that of the choice of filter construction for the wells which depends on the aquifer and the type of test to be completed. If the aquifer being tested is a very permeable coarse gravel and if the casing diameter is small, then simply numerous holes drilled in the solid casing may be adequate. In contrast, for a single-well test with an alternating cycle of injection and pumping of large volumes of water into and out of loose, fine-grained sand, an expensive well screen with a carefully placed gravel pack may be required. Regardless of the type of filter used, it is absolutely essential that the casing perforations, gravel pack, or screen as well as the aquifer at the well be cleaned of silt, clay, drilling mud, and other material which would prevent the free movement of water in and out of the well. This process of cleaning or development is so critical that it should be specified in clear terms in any contract related to well construction.

Injection and Sample Collection

Injection equipment depends on the depth of the borehole and the funds available. In very shallow holes, the tracer can be lowered through a tube, placed in an ampule, which is lowered into the hole and broken, or just poured in. Mixing is desirable and important for most types of tests and is simple for very shallow holes. For example, a plunger can be surged up and down in the hole or the release of the tracer can be through a pipe with many perforations. Flanges on the outer part of the pipe will allow the tracer to be mixed by raising and lowering the pipe. For deeper holes, tracers must be injected under pressure and equipment can be quite sophisticated. See Figure 3.5 for an example of a high-pressure injection system. The interval of interest in the borehole is usually packed off. This equipment is often custom built for a specific experiment, as tracer injection systems for water wells are not yet available commercially. As mentioned before, instantaneous injection is the ideal condition. For a pulse test, this may mean an injection period of a minute or an hour, depending on the equipment. The equipment shown in Figure 3.5 is described in detail in Simpson et al. (1983) with details of work conducted in fractured rock by the Department of Hydrology at the University of Arizona.

Sample collection can also be simple or sophisticated. For tracing thermal pulses, only a thermistor needs to be lowered into the ground water (Figure 3.6). For chemical tracers at shallow depths, a hand pump may be sufficient. Bailers can also be used, but they mix the tracer in the borehole which for some purposes should be avoided. A TEFLON bottom-loading bailer is described in Buss and Bundt (1981). It may be desirable to clear the borehole before taking a sample, in which case a gas-drive pump can be

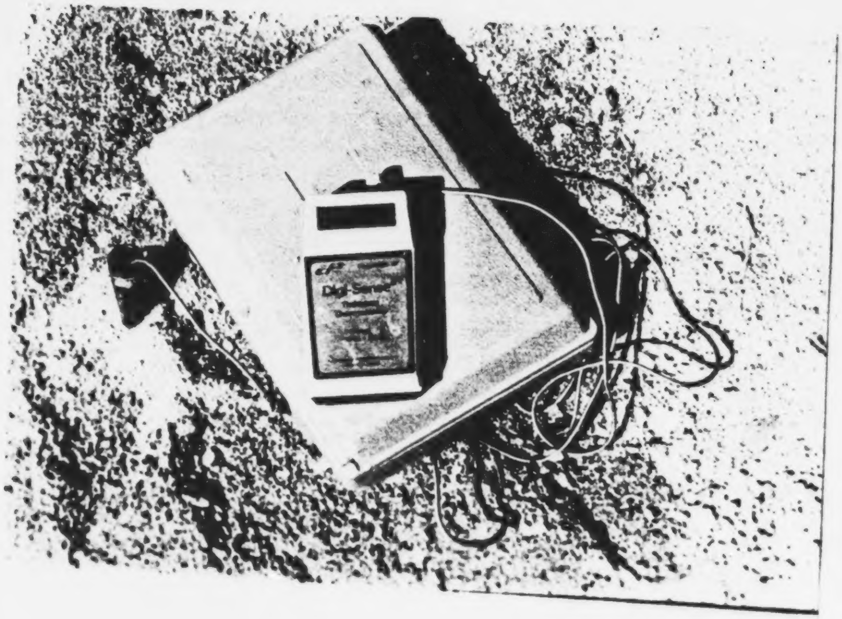


Figure 3.6a. Small digital thermometer with thermistor line in observation well. A thermal pulse produced by injecting warm water is being measured at this point.

Figure 3.6b. Recording data from test. Although thermistor signals are easily recorded automatically, hand recording is satisfactory for many low-budget, short-term tests.

used to evacuate the well. For a nonpumping system, the decision as to how much water must be withdrawn from a borehole in order to obtain a sample which is representative of the water adjacent to the borehole is not a trivial problem. If not enough water is taken out, the sample composition will be influenced by semistatic water which will normally fill much of the well. If too much water is drawn out, a gradient towards the well will be created and the natural movement of the tracer will be distorted. A common rule of thumb is to pump out four times the volume of water which is in the well before the sample is taken (see Figure 3.7).

If existing wells which have been drilled for water-supply purposes are used for tracer tests, extreme care is required because of the complex relationship among such variables as pumping rates, patterns of water circulation lation within the well, and the yields of different parts of the aquifers which are penetrated. This complexity is reflected commonly in the variability of water chemistry as a well is being pumped (Keith et al., 1982; Schmidt, 1977). Stated simply, for wells drawing water from complex aquifers or a series of aquifers, an analysis of a single water sample taken at a given point in time cannot yield definitive information about the water chemistry of any individual zone.

Many systems for sampling in wells have been described in recent years. Ground Water Monitoring Review is a good source of current techniques. Multi-level samplers are described in this journal by Cherry and Johnson (1982) and Pickens et al. (1981). For more information on gas-driven and positive displacement sampling devices, see Robin et al. (1982), Morrison and Brewer (1981), and Gillham and Johnson (1981).

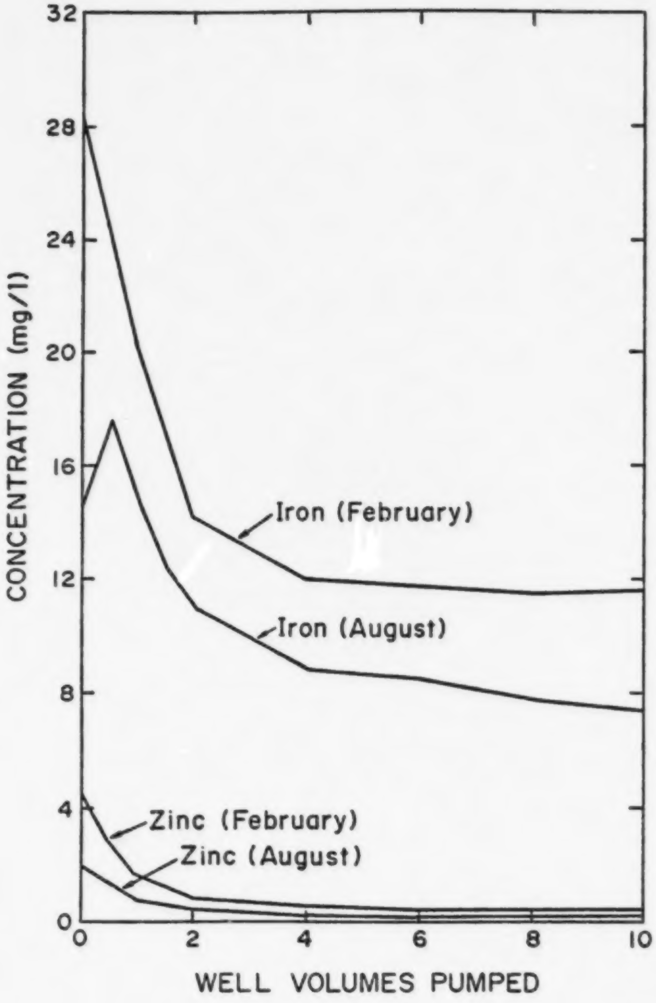


Figure 3.7. A difficult problem in field tests is to obtain a representative sample from an open test hole. Results of the analyses of successive samples taken from a small test hole are shown in this diagram which show that useful samples appear to be obtained after pumping 4 well volumes out of the hole. However, the number of well volumes needed varies with the hydraulic gradient, the well construction, the permeability of the zone being sampled, the type of tracer used, and the volume of water initially in the well. Diagram is adapted from Gibb, Schuller, and Griffin (1981).

The preservation and analysis of samples is covered in Chapter Four and Appendix C. Keith et al. (1982) also cover some of the practical problems involved with sample collection, analyses, and quality control.

Interpretation of Results

The following remarks and figures are intended only as a brief qualitative introduction to the interpretation of the results of tracer tests. More extensive and quantitative treatments are found in the works of such authors as Halevy and Nir (1962), Theis (1963), Fried (1975), Custodio (1976), Sauty (1978), Grisak and Pickens (1981), and Gelhar (1982).

The basic plot of the concentration of a tracer as a function of time or water volume passed through the system is called a breakthrough curve. The concentration is either plotted as the actual concentration (Figure 3.2) or, quite commonly, as the ratio of the measured tracer concentration at the sampling point, C, to the input tracer concentration, C_0 (Figure 3.8).

The measured quantity which is fundamental for most tracer tests is the first arrival time of the tracer as it goes from an injection point to a sampling point. The first arrival time conveys at least two bits of information. First, it indicates that a connection for ground-water flow actually exists between the two points. For many tracer tests, particularly in karst regions, this is all the information which is desired. Second, an approximation of the maximum velocity of ground-water flow between the two points may be obtained if the tracer used is conservative.

Interpretations more elaborate than the two simple ones mentioned depend very much on the type of aquifer being tested, the velocity of ground-water flow, the configuration of the tracer injection and sampling systems, and the type of tracer or mixture of tracers used in the test.

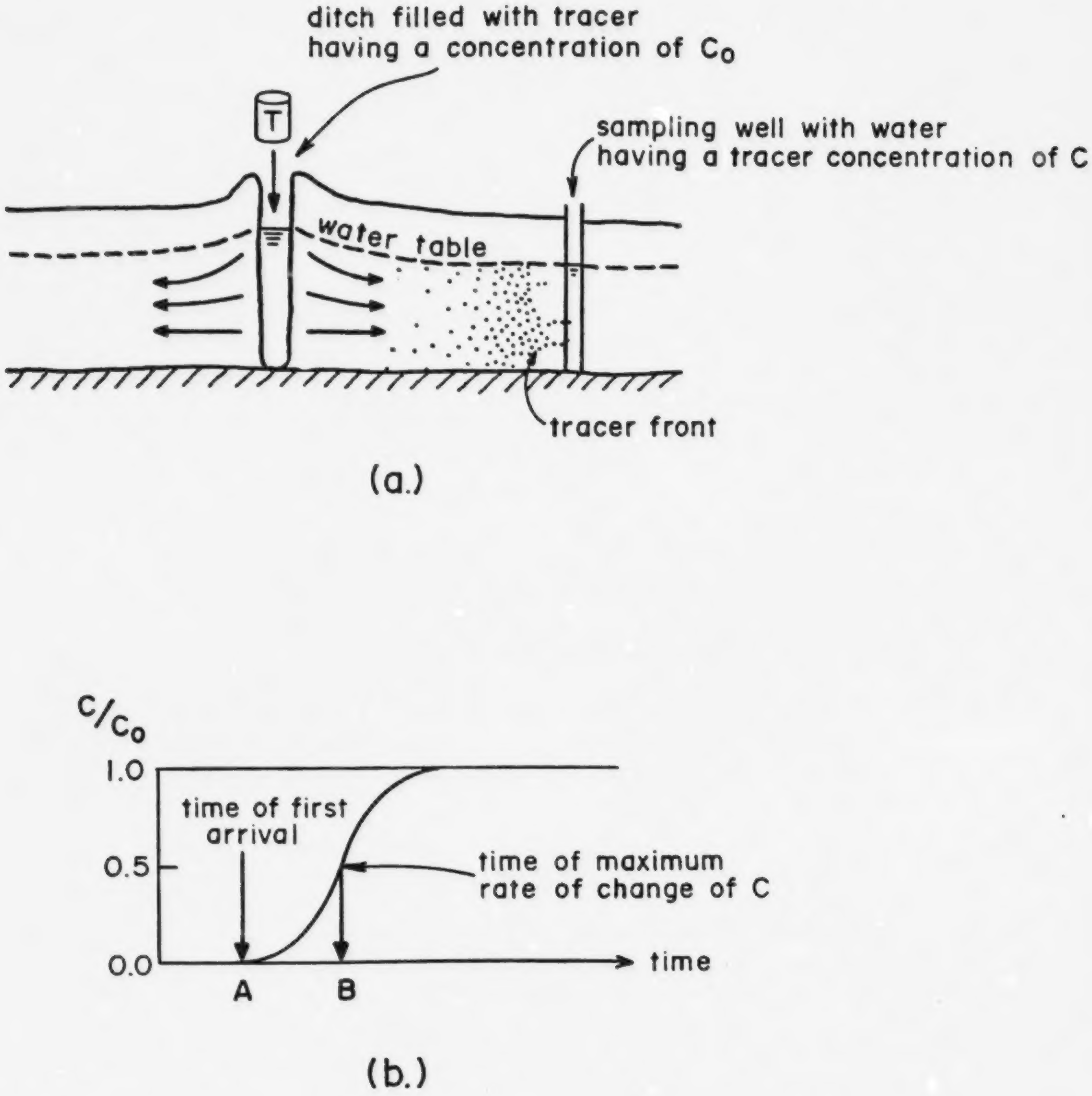

ditch filled with tracer
having a concentration of C_0
T
sampling well with water
having a tracer concentration of C
water table
tracer front
(a.)
C/C_0
1.0
0.5
0.0
time of first
arrival
time of maximum
rate of change of C
time
A
B
(b.)

Figure 3.8(a). Ditch into which a tracer is injected continuously and mixed with the water in the ditch to produce water with an initial fixed tracer concentration of C_0. The arrival of the tracer front is studied by taking samples from the well that is downgradient from the ditch. (b) The breakthrough curve obtained from injecting tracers into the ditch.

Next after the first arrival time, the most interest is commonly centered on the arrival time of the peak concentration for a slug injection, or for a continuous feed of tracers, the time since injection when the concentration of the tracer changes most rapidly as a function of time (Figure 3.8). In general, if conservative tracers are used, this time is close to the theoretical transit time of an average molecule of ground water traveling between the two points. The "spread" of the curve is also of interest. The "spread" can be related to the combined effects of hydrodynamic dispersion and molecular diffusion (Figure 3.9).

If a tracer is being introduced continuously into a ditch penetrating an aquifer as shown in Figure 3.8, then the ratio C/C_0 will approach 1.0 after the tracer starts to pass the sampling point. The ratio of 1.0 is rarely approached in most tracer tests in the field, however, because waters are mixed by dispersion and diffusion in the aquifer and because wells used for sampling will commonly intercept far more ground water than has been tagged by tracers (Figure 3.10). Ratios of C/C_0 in the range of between 10^{-5} and 2×10^{-1} are often reported from field tests.

If a tracer is introduced passively into an aquifer but is recovered by pumping a separate sampling well, then various mixtures of the tracer and the native ground water will be recovered depending on the amount of water pumped, the transmissivity of the aquifer, the slope of the water table, and the shape of the tracer plume. Keely (1984) has presented this problem graphically with regards to the removal of contaminated water from an aquifer.

With an introduction of a mixture of tracers, possible interactions between the tracers and the solid part of the aquifer may be studied. If

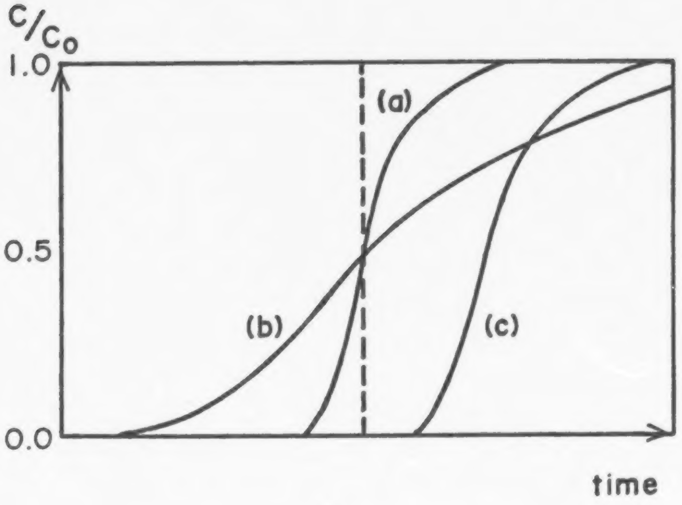


Figure 3.9. Breakthrough curves a and b were obtained from tests in two different media. Test a shows only a moderate amount of dispersion while test b shows a rather high amount of dispersion. Tests a and c were conducted at the same time in the same material but with different tracers. The displacement of the test curve c to the right of the diagram is caused by sorption of the tracer on the solid material in contact with the water.

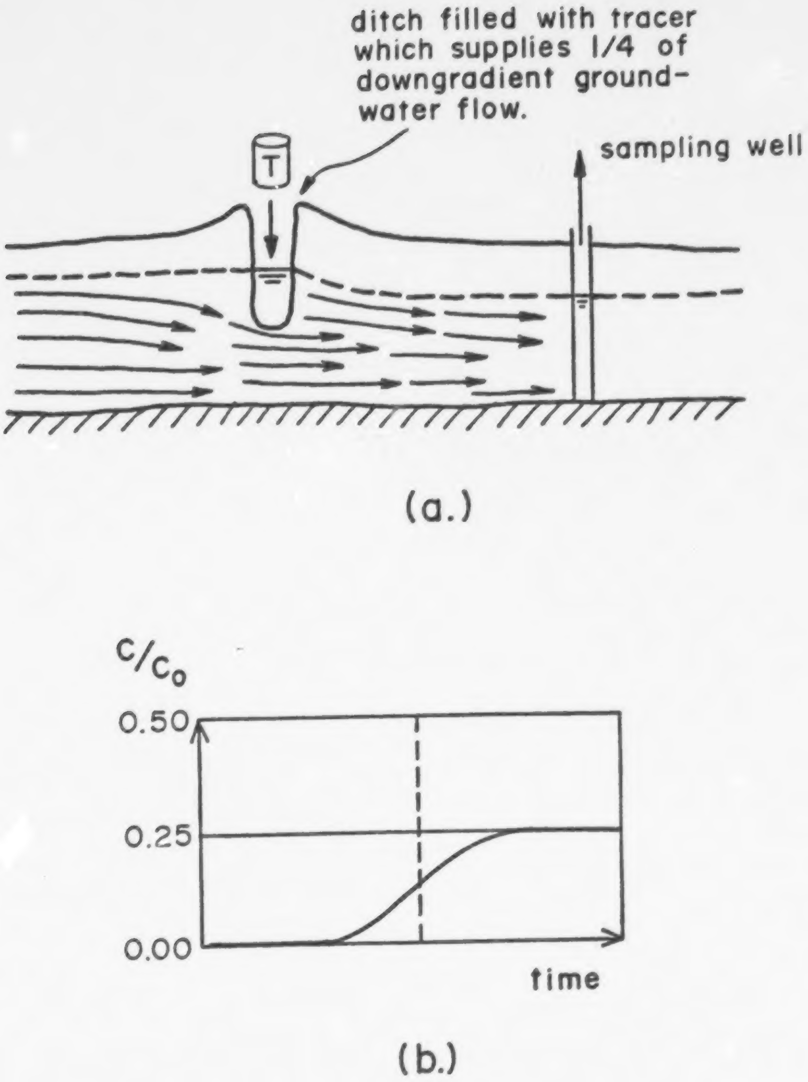

ditch filled with tracer which supplies 1/4 of downgradient ground-water flow.
T
sampling well
(a.)
C/Co
0.50
0.25
0.00
time
(b.)

Figure 3.10. Most tracer tests do not fully saturate the aquifer with the tracer being injected. This is shown in diagram (a). The resulting breakthrough curve, diagram (b), therefore, will never increase to the C/C_o value of 1.0.

interactions take place, they can be detected by comparing breakthrough curves of a conservative tracer with the curves of the other tracers being tested (Figure 3.11). A common strategy for these types of tracer tests is to inject and subsequently remove the water containing mixed tracers from a single well. If injection is rapid and pumping to remove the tracer follows right away, then a recovery of almost all the injected conservative tracer is possible. If the pumping is delayed, the injected tracer will drift downgradient with the general flow of the ground water and the percentage of the recovery of the conservative tracer will be less as time progresses. Successive tests using longer delay times between injection and pumping is one qualitative method to estimate ground-water velocities in permeable aquifers with moderately large hydraulic gradients.

The methods of quantitative analyses of tracer breakthrough curves are generally by curve-matching of computer-generated type curves, or by analytical methods. Analytical methods are covered in Fried (1975). Sauty (1978) provided solutions for solute transport for different flow fields (linear and radial) and for diverging and converging conditions. He covered continuous and slug injection. Sauty (1978) presented a finite difference method to be used with converging and diverging problems; the program is called RAMSES. Carrera and Walter (1985, manuscript in preparation) developed a similar, more accurate program called CONFLO for use in converging problem.

An example of a type curve is given in Figure 3.12. The match can be done by eye or by computer.

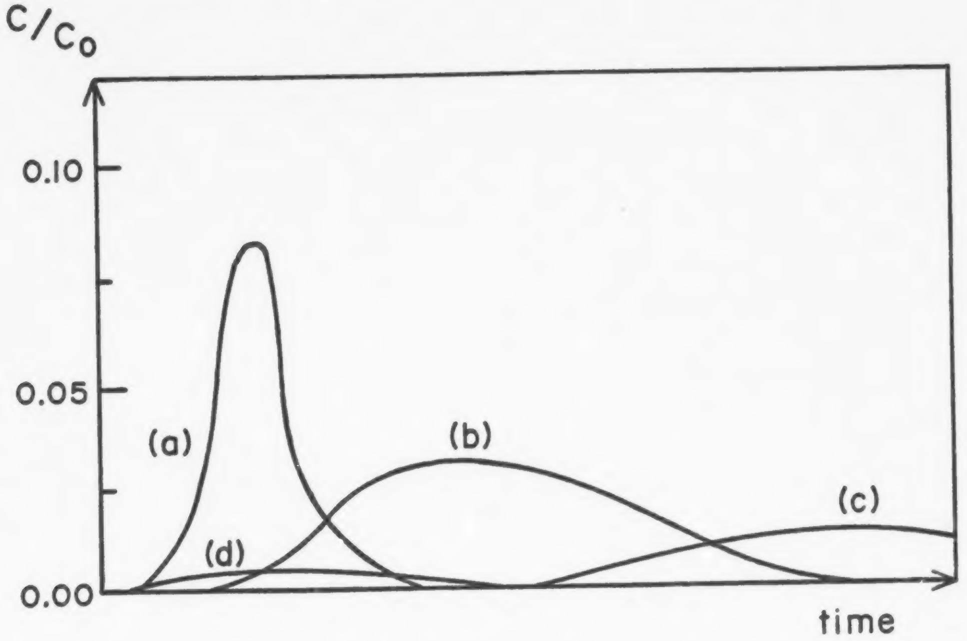


Figure 3.11. In this hypothetical diagram, four different tracers are mixed and injected as a single slug into an aquifer. As can be seen in the resulting breakthrough curves, tracer a is conservative, tracer b shows some effect of sorption on the aquifer, tracer c shows a large effect of sorption, and tracer d is precipitated or destroyed before a significant amount reaches the sampling point. The destruction can be by radioactive decay, by chemical decomposition, or by the metabolic action of microorganisms.

Figure 3.12. Computer-generated type curves are used for a two-well test in which one well is used for injection and the other for sampling to find dispersivity (α) and porosity (ϕ). The vertical axis is dimensionless concentration, defined as the following:

$$C_D = \frac{\pi r^2 b \phi C}{m} \qquad (8)$$

where $\pi r^2 b\phi$ = volume of the cylinder defined by the injection and withdrawal of wells;

b = thickness of aquifer;

r = distance between wells;

C = measured concentration at time t;

M = mass of tracer injected during the test.

The horizontal axis is reduced time, defined as:

$$t_R = \frac{tQ}{\pi r^2 b \phi} \qquad (9)$$

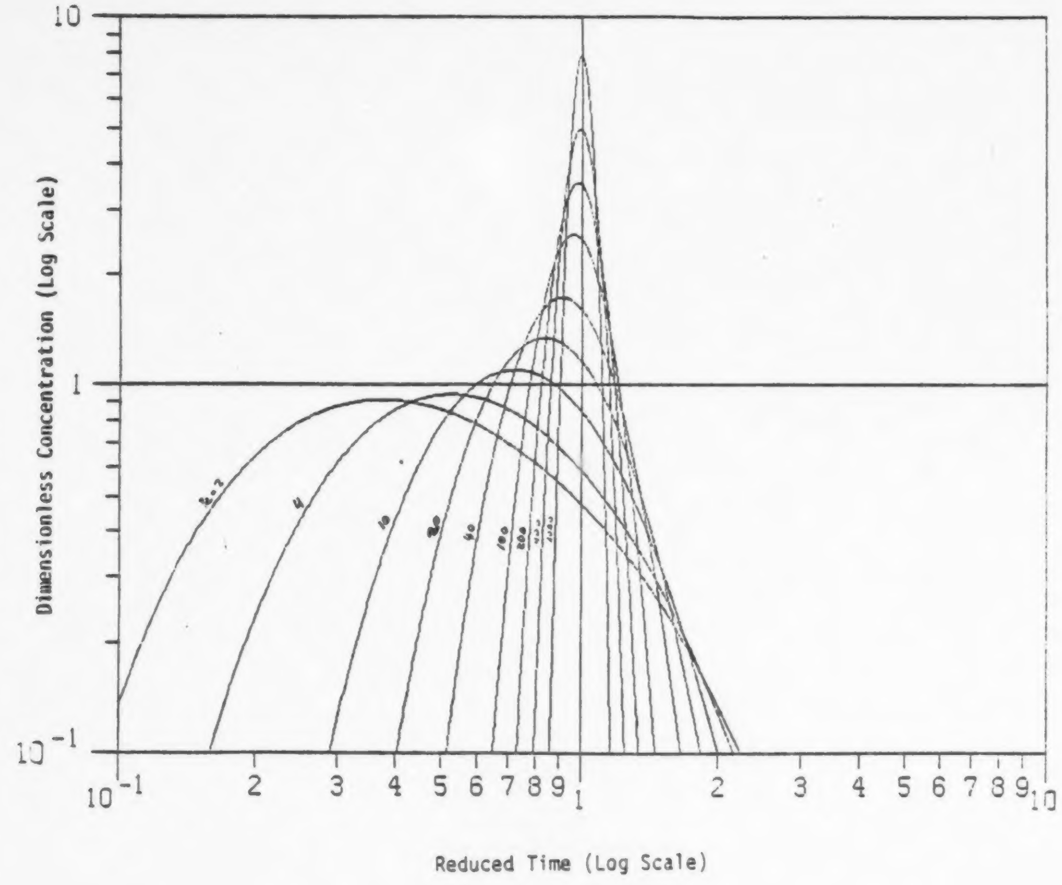
where t = time of sampling;

Q = pumping rate.

When analyzing a test, the tracer test results are plotted as log C versus log t on the vertical and horizontal axes, respectively. The experimental curve is matched with a type curve, keeping axes parallel. From the match curve, the Peclet number is found. The Peclet number (Pe) is equal to r/α, so the dispersivity is obtained. Next, a match point is chosen for any point on both curves. The equation for reduced time is used, and all values except ϕ are known. Then,

$$Q = \frac{Q_t}{\pi r^2 b t_R} \qquad (10)$$

To verify the validity of the method, the dimensionless concentration equation is used. From the matchpoint, C and C_D are known. If $C_D = \frac{\pi r^2 b \phi C}{m}$, the method has been has been verified. These type curves were developed by HydroGeoChem, Inc., of Tucson, Arizona, 1984.


10
1
10^{-1}
Dimensionless Concentration (Log Scale)
10^{-1}
2
3
4
5
6
7
8
9
1
2
3
4
5
6
7
8
9
10
Reduced Time (Log Scale)
2
4
10
20
40
100
200
400
1000

CHAPTER FOUR

TYPES OF TRACERS

In this chapter, information is presented concerning various types of tracers, including water temperature, solid particles (yeast, bacteria, spores, etc.), ions, organic acids, dyes, and radioactive tracers. The final section of the chapter deals with environmental tracers, such as stable isotopes and radionuclides. Each tracer type will be discussed regarding its applicability in different hydrologic settings, the field methods ods used (necessary equipment and sampling techniques), and type of detection used. Additional information (interpretation of results, cost of the tracer, and environmental and health concerns) is presented at the conclusion of each subsection.

Temperature

The temperature of water changes slowly as it migrates through the subsurface, because water has a high specific heat capacity compared to most natural materials. For example, temperature anomalies associated with the spreading of warm wastewater in the Hanford Reservation in south-central Washington have been detected more than 8 km (5 miles) from the source (U.S. Research and Development Adm., 1975).

Water temperature is a potentially useful tracer, although it has not been used frequently. The method should be applicable in granular media, fractured rock, or karst regions. Keys and Brown (1978) traced thermal pulses resulting from the artificial recharge of playa lake water into the Ogallala Formation in Texas. They described the use of temperature logs (temperature measurements at intervals in cased holes) as a means of detecting hydraulic conductivity differences in an aquifer. Temperature logs have also been used to determine vertical movement of water in a borehole (Keys and MacCary, 1971; Sorey, 1971).

Heat is transmitted by convection (transport of heat by fluid flow) and conduction (due to temperature gradients within the saturated material). Assuming that convection dominates, Keys and Brown (1978) demonstrated the use of a simple temperature model to estimate a ratio of 1:3 for the velocity of the temperature pulse compared to the water velocity in a granular material. The actual ratio depends on aquifer porosity, density of the aquifer material and of water, and the heat capacity of the aquifer material and of water. They concluded that the actual relationship between the rate of transmission of a thermal wave in an aquifer and the velocity of water was unknown. However, water most certainly has a higher velocity than the temperature pulse.

Laboratory column tests have been performed to compare the travel times of chloride, yeast, and temperature (Keys and Brown, 1978). The chloride concentration began to increase at 0.8 pore volumes and reached input concentration at 1.2 pore volumes. The yeast began to increase at 0.95 pore volumes and reached input concentration at 1.25 pore volumes. Temperature began to rise at 0.7 pore volumes and reached input temperature at 3.25 pore volumes. The heat traveled faster than the other tracers as far as initial detection is concerned, but the center of mass of the thermal pulse arrived later than the chloride or yeast. This illustrates the point that changes in water temperature are accompanied by changes in density and viscosity of the water. This, in turn, alters the velocity and direction of flow of the water. For example, injected ground water with a temperature of 40°C will travel more than twice as fast in the same aquifer under the same hydraulic gradient as will water at 5°C. Because the warm water has a slightly lower density than cold water, buoyant forces give rise to flow which "floats" on top of the cold water. In order to minimize problems of temperature-induced convection, small temperature differences with very accurate temperature measurements should be used if hot or cold water is the introduced tracer.

Temperature was used as a tracer for small-scale field tests, using shallow drive-point wells two feet apart in an alluvial aquifer. The transit time of the peak temperature was about 107 minutes, while the resistivity data indicate a travel time of about 120 minutes (see Figure 4.1). The injected water had a temperature of 38°C, while the ground-water temperature was 20°C. The peak temperature obtained in the observation well was 27°C.

In these tests, temperature served as an indicator of breakthrough of the chemical tracers, aiding in the timing of sampling. It was also useful as a simple, inexpensive tracer for determining the correct placement of sampling wells.

The use of cold water as an injected tracer was attempted by Simpson (personal communication, 1984). Icicles of water containing I^{131} were deposited in a borehole penetrating an alluvial aquifer. No temperature or radiation change was detected at sampling points, while breakthrough did occur when the liquid tracer was used. The higher density of the cooler tracer is believed to have caused the tracer to sink and miss the sampling points.

Another application of water-temperature tracing is the detection of river recharge in an aquifer. Most rivers have large water temperature

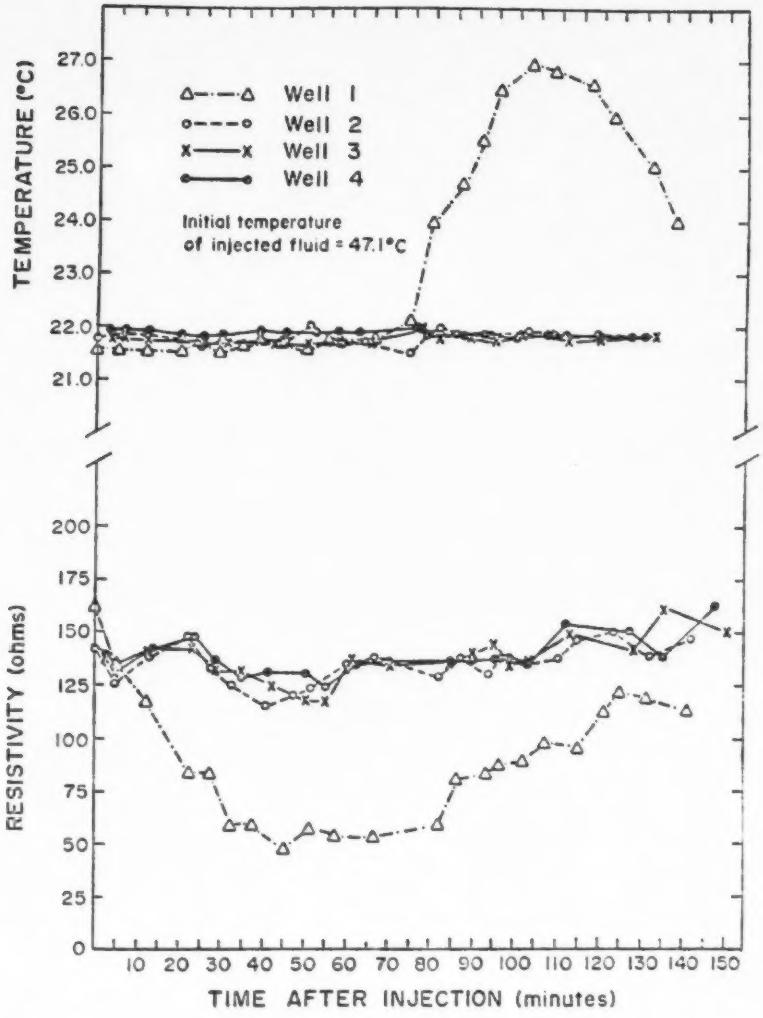


Figure 4.1. Results of a field test in which hot water was injected into a well in a shallow aquifer of coarse alluvium. The sampling wells were perforated metal pipes driven two feet from the injection well and arranged in a semicircle in the downstream direction. Only Well #1 intercepted the injected water, thus establishing the local direction of ground-water flow. Resistivity of the aquifer was measured between the injection well and the sampling wells by passing a small electrical current under a 6v potential from the injection well to the various sampling wells. The lowering of resistivity caused by the hot water verifies the flow direction which was determined by measuring water temperatures. Because the resistivity of the entire volume of the aquifer between the wells is measured, the initial drop in resistivity does not signal the arrival of the hot water in Well #1; it simply indicates that the hot water was started on its way towards Well #1.

fluctuations in response to seasonal effects. If the river is recharging an aquifer, the seasonal fluctuations can be detected in the ground water adjacent to the river (Rorabaugh, 1956).

- Field Methods

One of the attractive aspects of the use of temperature as a tracer is the relatively simple and inexpensive equipment required. Temperature is usually measured by means of a temperature probe, which utilizes a thermistor. The instrument measures resistance, which is converted to temperature ature electronically or manually by a calibration curve. The probes are available with meters or with digital readouts. Recording devices can be attached, and logs may be in analog or digital form.

Any of the tracer test types (see Chapter 4) could theoretically be used. The tests performed by Keys and Brown (1978) were natural gradient tests, with pressure injection. The authors also used a natural gradient test. A short-term test using natural gradients has not been used successfully for a travel distance greater than 46 meters. Plumes of warm water have been documented at many places where there has been a constant feed of warm water into an aquifer over periods of many years.

The logging method requires movement of the probe up and down in the borehole. An alternative is to leave the probe at a constant depth, which yields an average travel velocity for a small interval of the aquifer above and below the sampling point.

- Detection and Analysis

The lack of laboratory analyses and the easy means of obtaining direct measurements in the field are advantages of using a thermal tracer. Temperature can be detected in sealed pipes, while chemical, bacterial, and particulate tracers are generally sampled and identified after entering a borehole from a screened segment. This makes multi-level sampling for non-thermal tracers more difficult, and a vertical distribution of tracers is seldom obtained.

Temperature measurements can be quite sensitive using modern equipment. Keys and Brown (1978) used a probe with an accuracy, repeatability, and sensitivity of approximately 0.02°C. With very expensive temperature detection equipment, this performance can probably be improved by an order of magnitude.

- Additional Information

The velocity measurements obtained from temperature tests are generally not equal to water velocity, as discussed previously. A conservative tracer such as chloride could be used to determine the temperature lag for site-specific tests. Temperature is currently most useful in obtaining relative velocities of various zones within an aquifer.

The expenses involved in this type of test are minimal in comparison to other tracer tests. A relatively inexpensive probe and a recording device (if desired) are the only capital expenses. Labor is minimized due to the lack of laboratory analyses.

Environmental effects should not be a problem in this type of test provided high quality water is used for injection. For more information on temperature as a ground-water tracer, see Stallman (1963), Sorey (1971), and Combarnous and Bories (1975).

Solid Particles

Solid material in suspension can be a useful tracer in areas where water flows in large conduits, such as some basalt, limestone, or dolomite aquifers. Aley (1976) reported that geese, bales of hay, and wheat chaff have been used in Missouri in karst regions. In the past decade, small particulate tracers such as bacteria have been used successfully in porous media.

This section of the manual will briefly describe the following particulate tracers; paper and simple floats, signal-emitting floats, yeast, bacteria, viruses, and spores.

Paper and Simple Floats

Some examples of these tracers are small bits of paper (as punched out from computer cards, for example), or multicolored polypropylene floats. Due to the large size of these tracers, they are useful only when flow is through large passages. The particles must be of such a size and density as to pass through shallow sections of flow without settling out. Because these particulates generally float on the surface, they travel faster than the water's mean velocity. These tracers are most useful for approximating the flow velocity and establishing the flow path.

Dunn (1963, 1963) described the use of polypropylene floats of approximately 3/32-inch diameter and one-inch length.

• Field Methods

This type of test requires very little equipment. The tracer is introduced in a sinkhole or other convenient locations and is recovered by sieving water as it emerges from springs or karst openings.

• Detection

The particulates are counted manually.

• Additional Information

This method is very inexpensive. Environmental effects are minimal.

Signal-Emitting Floats

A novel tracer is a small delayed time bomb which floats through a cave system. When the bomb explodes, the location of the explosion is determined by seismic methods at the surface (Arandjelovic, 1969 and 1977). W.A. Schnitzer (1972) described karst tracing experiments in which blasting takes place in dolines. Sound impulses are detected by microphones in adjacent springs. The impulses can be recorded by oscillographs. Another method of tracing underground streams is described by Lange (1972). The method utilizes natural noise impulses generated by moving water. The signal is detected on the surface by seismometers, then amplified and recorded on magnetic tape or on a chart recorder. It combines an acoustic tracking method and a procedure used by seismologists to locate the foci of earthquakes. Problems with this method include noise interference from wind, traffic, and surface streams.

Because these methods are relatively expensive and have seldom been used, they will not be discussed in further detail.

Yeast

The use of baker's yeast (*Saccharomyces cerevisiae*) as a ground-water tracer in a sand and gravel aquifer has been reported by Wood and Ehrlich (1978). Yeast is a single-celled fungus which is ovoid in shape. The diameter of a yeast cell is 2 to 3 μm, which closely approximates the size of pathogenic bacterial cells. This tracer is probably most applicable in providing information concerning the potential movement of bacteria.

- Field Methods

In Wood and Ehrlich's experiments, tracer tests were conducted in wells located 1.50 m (5 feet) apart. However, the tracer was detected at an observation well 7.6 m (25 feet) down-gradient. The injection concentration was 16 kg (35 pounds) of baker's yeast to 45 l (12.8 gallons) of water.

Samples for yeast analysis can be collected in sterile bottles at regular intervals and prepared for analysis in the field.

- Detection/Sample Analysis

The samples must first be filtered through membrane filters. The filters are then placed on absorbent pads saturated with M-Green Yeast and Mold Broth and incubated at 30°C for 36 hours. Colonies can then be counted under low magnification. This type of analysis is fairly simple, relatively inexpensive, and requires little specialized equipment, other than a source of heat for incubation. A wide range of concentrations can be analyzed because the sample can be diluted if the colonies are too numerous to count. One advantage of yeast is negligible background levels.

- Additional Information

Wood and Ehrlich (1976) found that the yeast penetrated more than 7 meters into a sand and gravel aquifer in less than 48 hours after injection. The relative mobilities of yeast and chloride were also compared in this study. Yeast cells are generally mechanically filtered as they pass through the intergranular pore space. It appears that microbial cells such as yeast or bacteria become trapped at the soil-water interface (e.g., of an injection well), and as the mat of cells increases, it becomes a more effective filter (Vecchioli et al., 1972). This causes the breakthrough curve to increase to an abrupt maximum and then decrease sharply (see Figure 4.2).

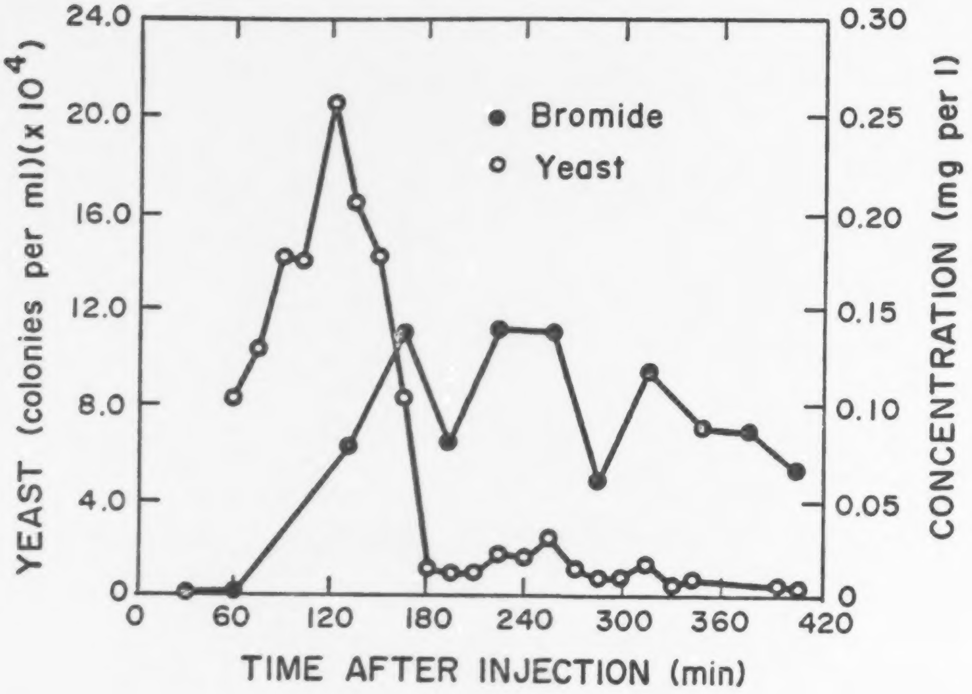


Figure 4.2. Results of a two-well tracer test in an alluvial aquifer using bromide and yeast. Although the bulk of the yeast was probably filtered out, some particles moved through the largest openings to produce an early breakthrough peak on the graph. This apparent anomaly where a nonconservative particulate tracer arrives ahead of the bulk of the conservative tracer is caused by the fact that the largest openings which carry the particles are also the paths of highest velocities. (Graph is redrawn from Wood and Ehrlich, 1978).

In Wood and Ehrlich's study, the yeast arrived faster than the conservative ionic tracers, bromide and iodide.

In this case, the time lag in the peak concentrations of bromide and iodide was due to their flow occurring simultaneously in solution channels and intergranular pores. The yeast cells are believed to have traveled through the solution openings. The cells were probably filtered from suspension, and did not flow through the intergranular pores. The two types of flow would explain the abrupt peak for yeast and gradual rise and long tail for bromide.

The tracer is very inexpensive, as is analysis. The lack of environmental concerns related to this tracer is one of its advantages.

Bacteria

Bacteria are the most commonly used microbial tracers, due to their ease of growth and simple detection. Recently, Keswick et al. (1982) reviewed case studies of bacteria used as tracers. Some of the bacteria which have been used successfully are *Escherichia coliform* (E. coli), *Streptococcus faecalis*, *Bacillus stearothermophilus*, *Serratia marcescens*, and *Seratia indica*. They range in size from one to ten microns and have been used in a variety of applications.

A fecal coliform, E. coli, has been used to indicate fecal pollution at pit latrines, septic fields, and sewage disposal sites. A "marker" such as antibiotic resistance or H_2S production is necessary to distinguish the tracer from background organisms. Hagedorn et al. (1978) and Rahe et al. (1978) used antibiotic-resistant strains of E. coli and *Streptococcus faecalis* to trace movement through a saturated soil. Bacteria movement through fractured bedrock was studied by Allen and Morrison (1973). Rippon (1963) used a bacterial tracer for detecting water movement in an estuary, and Wimpenny et al. (1972) used an antibiotic strain of *Serratia marcescens* as a tracer in a polluted river.

- Field Methods

Most bacterial tracer tests reported in the literature are two-well natural gradient tests. The tracer can be injected by siphoning from the container, through Tygon tubing, to the desired depth. Injection under pressure has been used. The wells may be relatively far apart, as Sinton (1980) reported recovery at a distance of 920 meters.

The samples can be obtained by bailer or hand pump. Most workers place the samples on ice and transport them to the laboratory. Samples should then be stored at 4°C or otherwise refrigerated until analyzed.

- Detection

As mentioned previously, some type of "marker" (such as antibiotic resistance) is necessary to distinguish tracer bacteria from background bacteria, that are almost always present.

The average time for lab analysis is one to two days. Cells are recovered from the water sample by membrane filtration, and the bacteria are then diluted by serial dilution, if necessary. The filters are incubated on plates of agar. A normal temperature is 37°C, and the time required ranges from 24 to 48 hours. Colonies are counted under low magnification.

Methods for growing inoculum (bacteria) for use as a tracer are described in Ormerod (1964), Rahe et al. (1978), and Sinton (1980).

- Additional Information

In choosing a bacterial tracer, a reasonable survival rate, with no reproduction, is desired. Some bacteria are capable of growth in aquifers, yielding erroneous tracer results. Another factor causing ambiguous results is the fact that bacteria, like yeast cells, are large enough to be filtered by some soils. Also, they may adsorb to a variety of surfaces. However, in field tests, bacterial tracers show faster transit times than dyes (Pyle, 1981; Rahe, 1978). Figure 4.3 illustrates relative travel times.

The tracer itself is relatively inexpensive, but may be difficult to obtain. The most obvious remedy is to culture the bacteria personally. Analysis requires a laboratory, incubator, and microscope. Cost (if samples are sent to a commercial laboratory) is comparable to a chemical analysis.

The greatest health concern in using these tracers is that the bacteria must be nonpathogenic to man. Even E. coli has strains which can be pathogenic. Davis et al. (1970) reported that *Serratia marcescens* may be pathogenic.

Another concern is related to the injection of antibiotic-resistant strains. The antibiotic resistance can be transferred to potential human pathogens. This can be avoided by using bacteria which cannot transfer this genetic information. As is true with most other injected tracers, permission to use bacterial tracers should be obtained from the proper federal, state, and local health authorities.

For more information concerning bacterial tracers, see Schaub (1977), Vecchioli (1972), Ormerod (1964), and Romero (1970).

Viruses

Animal, plant, and bacterial viruses have been recently used as groundwater tracers. Viruses are generally much smaller than bacteria, ranging from 0.2 to 1.0 microns (see Table 4.1). In general, human enteric viruses cannot be used, due to disease potential. Certain vaccine strains, such as

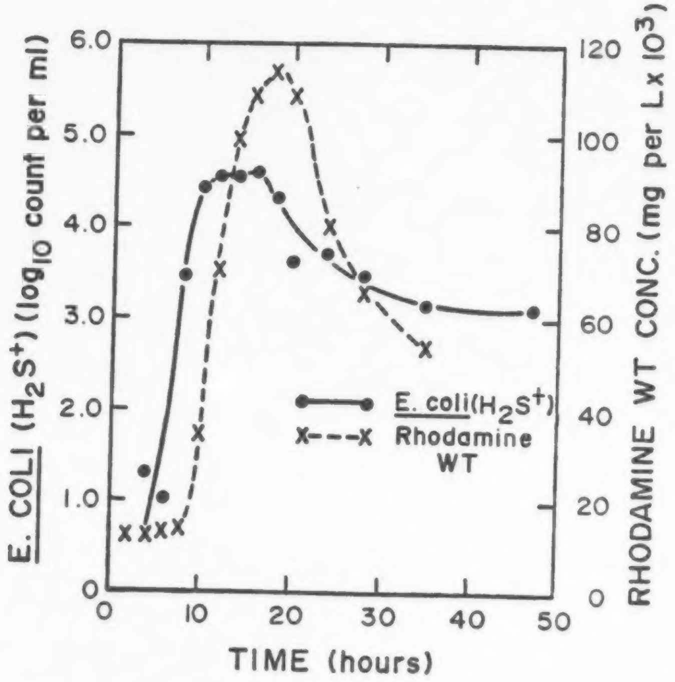


Figure 4.3. A comparison of travel time in a two-well tracer test using rhodamine WT dye and E. coli. The E. coli, which is a particulate tracer, arrived slight ahead of the dye, probably for reasons explained in connection with Figure 4.2. (Figure redrawn from Pyle and Thorpe, 1981).

TABLE 4.1

Comparison of Microbial Tracers

Tracer	Size (μm)	Time Required for Assay (days)	Essential Equipment Required
Bacteria	1-10	1-2	incubator[a]
Spores	25-33	1/2	microscope plankton nets
Yeast	2-3	1-2	incubator[a]
Viruses:			
Animal (enteric)	0.2-0.8	3-5	incubator tissue culture laboratory
Bacterial	0.2-1.0	1/2-1	incubator[a]

[a] Many may be assayed at room temperature.

a type of polio virus, have been used but are considered risky. Most animal enteric viruses are considered safer, as they are not known to infect man (Keswick et al., 1982). However, both human and animal viruses are generally not considered to be suitable tracers for field work. Bacterial viruses (bacteriophage) were first used by Wimpenny et al. (1972). Their properties are similar to those of animal viruses, but the health risk is lower. Virus tracers have several advantageous properties. The injection culture is easily grown in the laboratory. The viruses are specific to the host bacteria so that they may be mixed, injected, and then distinguished on different host bacteria. Also, viruses have shown good survival in groundwater studies.

The most useful application of virus tracers is in modeling the movement of microbial pathogens (such as hepatitis) in ground water. The movement ment of viruses from septic tank drainfields was traced with the use of a bovine enterovirus by Scandura and Sobsey (1981). In karst terrain in Missouri, Fletcher and Meyers (1974) used a bacteriophage which traveled a distance of 1600 meters. In granular media, the aquifer must be very permeable to observe long travel distances. Martin and Thomas (1974) used a bacteriophage in sandstone strata in South Wales, with a travel distance of 680 meters.

A possible use of virus tracers is in evaluating the suitability of potential land treatment sites (Keswick et al., 1982). A "standard" virus with well-defined properties could be used.

- Field Methods

An advantage of bacterial or virus tracers is the small injection volume needed to label large water volumes. A typical concentration of injected tracer might be 5×10^{10} phage per ml. In determining the injection quantity, Aley and Fletcher (1976) suggested that 97% of the tracer may be lost and noted that the minimum detection is 10 plaque-forming units per ml of water. The methods to prepare the tracer are described by Schaub et al. (1975) and Sargeant (1969). The stock to be injected can be grown relatively easily in a well-equipped microbiology laboratory in 10 to 24 hours.

The method used to assay viruses is described by Schaub and Sorber (1977), Schaub et al. (1975), and Aley and Fletcher (1976). In general, a portion of a sample is put on a plate of jelly-like bacteria. The plate is incubated for various lengths of time, depending on the bacteria and virus. The virus feeds off of the bacteria and leaves a clean area (plaque) of dead bacteria on the milky surface of the plate. The clear patches on the plate are counted manually, assuming that one phage is associated with one plaque. It is best to have 30-300 plaques per plate. The sample can be serially diluted to obtain this concentration.

The procedure is fairly complex and time consuming, and it may be difficult cult for hydrologists who generally lack knowledge of microbiological techniques.

An immunochemical type of virus assay (analysis) has the potential to reduce virus detection time to one to three hours (Keswick et al., 1982). However, this method is not yet available for water tracers.

- Additional Information

Some considerations in planning and interpreting virus tracer tests are die-off rates, background levels, and adsorption. The die-off rate should be investigated before choosing the tracer. Martin and Thomas (1974) found that the bacteriophage population which they used was reduced to 10% of the original value in about 28 days. The die-off rate is increased by higher temperature and exposure to ultraviolet light. Background levels of viruses in ground water might cause tracer test results to be incorrect and should be determined before the test. Aley and Fletcher (1976) described a method to determine if interfering bacteriophage are present in the water, which would infect the tracer phage's host bacteria.

Neglecting the time factor, the cost of using virus tracers is relatively small if access to a microbiology laboratory is available. The primary cost would be related directly to wages of laboratory personnel.

Spores

Lycopodium spores have been used as a water tracer since the early 1950's, and the techniques are well developed. Spore tracing was initiated by Mayr (1953) and Maurin and Zotl (1959). Their methods were modified by Drew (1968a). As is true with all larger particulate tracers, spores can be used only where significant interconnected large pores exist. Almost all applications of spore tracers have been in karst regions characterized by large solution openings in the aquifers.

Lycopodium is a clubmoss which has spores that are nearly spherical in shape, with a mean diameter of 33 microns. It is composed of cellulose and is slightly denser than water, requiring some turbulence to keep the material in suspension. Some advantages of lycopodium use are: (1) the spores are relatively small; (2) they are not affected by water chemistry or adsorbed by clay or silt; (3) they travel at approximately the velocity of the surrounding water; (4) the injection concentration can be very high (e.g., 8 x 10^6 spores per cubic centimeter); (5) no health threat is posed; (6) the spores are easily detectable under the microscope; and (7) at least five dye colors may be used, allowing five tracings to be conducted simultaneously in a karst system. Some disadvantages associated with its use include the large amount of time required for preparation and analysis of the spores, and the problem of filtering of spores by sand or gravel if flow is not sufficiently turbulent.

The basic procedure involves the addition of a few kilograms of dyed spores to a cave or sinking stream. The movement of the tracer is monitored by sampling downstream in the cave or at a spring, with plankton nets installed in the stream bed. The sediment caught in the net is concentrated, and treated to remove organic matter. The spores are then examined under the microscope.

Tracing by lycopodium spores is most useful in open joints or solution channels (karst terrain). It is not useful in wells or boreholes unless the water is pumped continuously to the surface and filtered. A velocity of a few miles per hour has been found sufficient to keep the spores in suspension. According to Smart and Smith (1976), lycopodium is preferable to dyes for use in large-scale water resource reconnaissance studies in karst areas. This holds if skilled personnel are available to sample and analyze the spores and a relatively small number of sampling sites are used.

The spores survive well in polluted water, but do not perform well in slow flow or in water with a high sediment concentration. Lycopodium spores have been used extensively in the United States, Great Britain, and other countries to determine flow paths and to estimate time of travel in karst systems.

• Field Methods

Various pieces of equipment are required for spore preparation, sampling, and analysis. Tracer preparation is described in detail in Drew and

Smith (1969), Gardner and Gray (1976), and Aley and Fletcher (1976). A respirator should be worn during the process, and extreme care must be used to avoid powder explosions when working with the dry spores. The spores and dyes can be obtained from a biological supply house (see Appendix D). The preparation involves heating the wetted spores, adding the dye and boiling for about an hour, and finally adding chemicals to fix the color in the spores. Next, the dyed spores are dried in an oven and refrigerated until used. The dyes found to be most easily distinguished with a regular microscope by Gardner and Gray (1976) were safranine orange, crystal violet, malachite green, sudan black, and crystal blue.

The equipment needed for sampling includes a conical plankton net and a trap (wood or metal frame) to hold the net. Nylon or silk nets are available from biological supply houses. Nylon is more expensive, but more tear-resistant than silk. A 25-micron mesh is generally used. One rule of thumb in determining the net opening diameter to be used is that the net opening should be no less than 10% of the cross-sectional area of flow at the location of the trap (Gardner and Gray, 1976). The nets are tapered at one end and fitted with a rubber tube and clip to allow emptying into a bottle during sampling.

Various suggestions have been made concerning injection quantity. A large quantity of spores is necessary because probably 99% of the injected spores are lost in transit, and only a few of those which are transported to the sampling site are caught in the nets. Drew and Smith (1969) and Atkinson (1968) recommended using 600 grams (dry weight) of spores (per 0.3 m^3/sec discharge) for every estimated kilometer of straight-line travel. This recommendation is based on the discharge of the largest spring and assumes that approximately 10% of the flow passes through the nets at the spring. A high silt content reduces the number of spores arriving at the sampling points. Maurin and Zotl (1959) used 2 to 3 kilograms for a discharge of 500-2,000 cubic meters per hour. Atkinson, Drew, and High (1967) used one kilogram of spores per 10,000 gallons per minute discharge, per mile of travel, with silk nets. With nylon nets, they successfully used 0.75 kilograms per 50,000 gallons per hour discharge, per mile of travel. Approximately 8-10% of the outflow was netted in this study.

The sampling nets must be installed before injection. The traps are placed securely in (see Figure 4.4) the portion of the stream or spring with the highest discharge. Extra traps should be available in case one is broken or lost.

Sampling consists of emptying the sediment trapped in the net into a bottle. The nets are washed in the stream and reused. The frequency of sampling will depend partly on the amount of sediment in the water, with a higher sediment load requiring more frequent sampling. If the purpose of the test is to determine where a sink resurges, sampling once every two days may be sufficient. If time of travel is desired, the interval should be no less than one-fifth of the estimated travel time (Gardner and Gray, 1976).

- Detection and Analysis

Laboratory analysis is fairly time consuming for this type of tracer experiment. The basic equipment includes a good quality microscope and a centrifuge. The analysis is described in detail in Aley and Fletcher (1976). Samples are filtered to separate the spores from larger solids, then concentrated with a centrifuge and analyzed under the microscope.

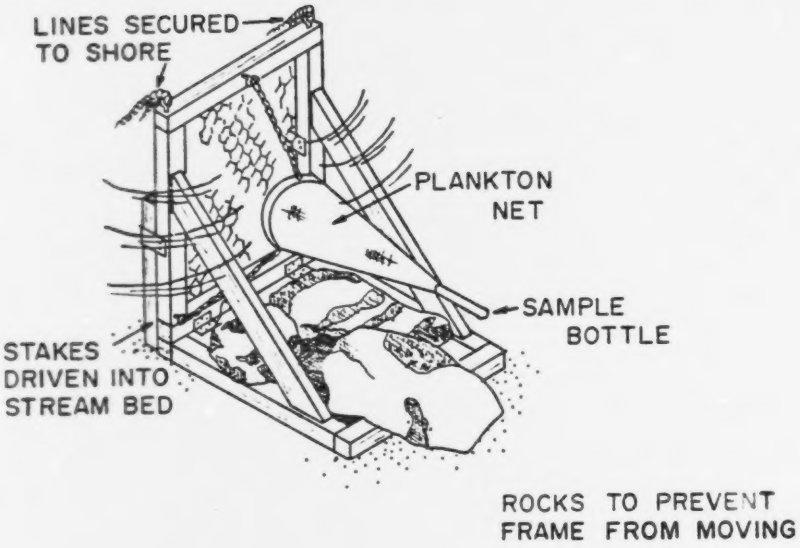

LINES SECURED TO SHORE
PLANKTON NET
SAMPLE BOTTLE
STAKES DRIVEN INTO STREAM BED
ROCKS TO PREVENT FRAME FROM MOVING

Figure 4.4. Tracing with spores is most commonly done in karst systems where cave streams or streams fed by large springs are available for sampling. Spores can be collected from the streams by anchoring a plankton net in the stream as shown in this sketch (adapted from Gardner and Gray, 1976).

Prevention of contamination is of utmost importance in the analysis lab. Analysis should not be performed in the same room in which spores were dyed.

- Additional Information

As mentioned above, contamination is the major concern in lycopodium tracing. Natural systems may have a background level, which should be tested for. Also, injected spores have been found in streams long after injection. If the time vs. concentration curve doesn't look reasonable, contamination is very likely. Gardner and Gray (1976) discussed precautions which should be taken to prevent contamination in all stages of spore preparation, injection, sampling, and analysis.

The performance of lycopodium in comparison to other tracers demonstrates its conservative nature. Buchtela et al. (1968) compared spores, uranine (a fluorescent dye) and sodium chloride, and found that lycopodium traveled most rapidly. This may be attributed to the fact that lycopodium stays in suspension only in fast, turbulent flow, so it probably travels faster than the average water velocity. Atkinson et al. (1973) compared lycopodium with pyranine, another fluorescent dye, and found similar peak arrival times (see Figure 4.5). However, the first arrival of lycopodium was much earlier than that of pyranine.

The cost of using lycopodium is generally considered greater than that of using dyes. Smart and Smith (1976) noted that capital costs are similar, but labor is higher for spore use. See Table 4.2 for a comparison of lycopodium and dye tracer properties.

Lycopodium is not associated with any known health effects, and it is considered one of the most harmless tracers.

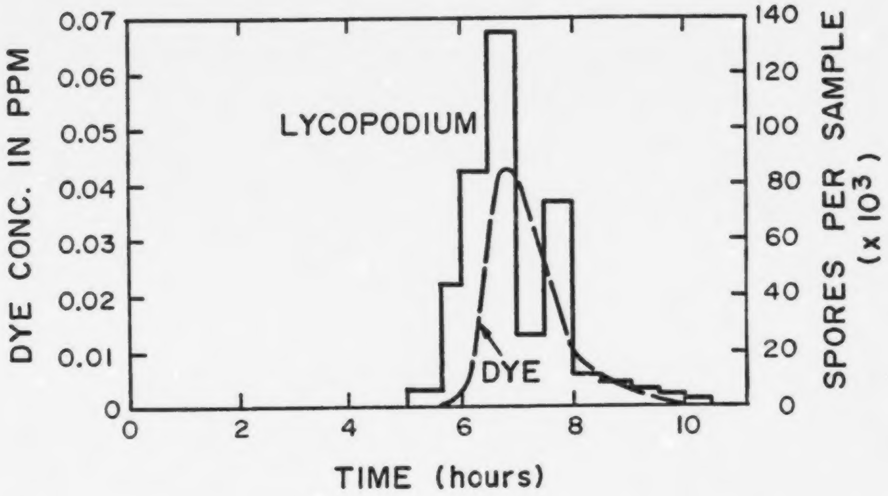


Figure 4.5. A comparison of the tracer pulse from lycopodium spores and a dye in a karst system (from Atkinson and Smart, 1978).

TABLE 4.2

Comparison of Lycopodium and Fluorescent Dye Properties

Lycopodium spores	Fluorescent dyes
Require only periodic sampling	Require frequent sampling
Sampling requires the use of special plankton nets	Sampling requires no special equipment and is possible using an automatic water sampler
Cost of capital equipment (microscope, centrifuge) moderate	Cost of capital equipment (fluorometer) high
Cost of non-capital equipment (nets, glassware, etc.) high	Cost of non-capital equipment (glassware) low
Pre-treatment to color spores time consuming and moderately expensive	No pre-treatment required
Post-collection treatment time consuming	No post-collection treatment
Analysis time consuming and requires skilled personnel	Analysis straightforward and fast, requires no skilled personnel
Immediate field analysis not possible	Immediate field analysis possible
Cost of tracers moderate	Cost of tracers moderate
Unaffected by water chemistry and pollutants	May be detrimentally affected by water chemistry and pollutants
Affected by high sediment concentrations	Affected only at extremely high sediment concentrations

Ions

Ionic compounds such as common salts have been used extensively as ground-water tracers. This category of tracers includes those compounds which undergo ionization in water, resulting in separation into charged elements possessing a positive charge (cations) or a negative charge (anions). The charge on an ion affects its movement through aquifers by numerous mechanisms, which will be discussed for each specific tracer. The ionic tracers which will be mentioned include chloride (Cl^-), bromide (Br^-), lithium (Li^+), ammonium (NH_4^+), magnesium (Mg^{++}), potassium (K^+), iodide (I^-), sulfate ($SO_4^=$), organic anions (such as benzoate), and fluorinated organic anions (such as M-TFMBA). Ions listed are those which have been found to be successful as tracers under various field and laboratory conditions.

Ionic tracers have been employed as tools for a wide range of hydrologic problems dealing with the determination of flow paths and residence time and the measurement of aquifer properties. Selection of the appropriate ionic tracer should be based on the purpose of the study; the type of aquifer system, such as karst, granular media, and fractured rock; the site specific aquifer characteristics, including the degree of heterogeneity and extent of clay lenses; the natural background concentration of specific ions in the ground water; and the analytical techniques available. The general characteristics of an ideal tracer have been outlined previously in the introduction. Specific characteristics of individual ions or ionic groups may approach those of an ideal tracer, particularly in the case of dilute concentrations of certain anions.

In most situations, anions (negatively-charged ions) are not affected by the aquifer medium. Mattson (1928), however, has shown that the capacity of clay minerals for holding anions increases with decreasing pH. Under such conditions of low pH, anions in the presence of clay, other minerals, or organic detrites may undergo anion exchange. Other effects which may occur include anion exclusion and precipitation/dissolution reactions. Cations (positively-charged ions), however, will react much more frequently with clay minerals through the process of cation exchange which in turn displaces other cations such as sodium and calcium into solution. For this reason, little work has been done with cations due to the interaction with the aquifer media. Versene (a tetra-sodium salt) has been used in the laboratory to prevent ion exchange (Haas, 1959). Kaufman (1956) has shown that when permeabilities and flow rates are low, often indicative of a large clay fraction, the solid phase may have a considerable capacity for adsorption of an ionic component. This is significant for cationic tracers and may have some significance for certain anionic tracers.

One advantage of the simple ionic tracers is that they do not decompose and thus are not lost from the system. One consideration in the application of specific ions is the background concentration of the tracer in the natural ground water or receiving waters. A large number of ions (including Cl^- and NO_3^-) have high natural background concentrations. Use of these ions under such situations would require the injection of a tracer of high concentration which may result in density separation and gravity segregation during the tracer test (Grisak, 1979). Density differences will alter flow patterns, the degree of ion exchange, and secondary chemical precipitation, which may change the aquifer permeability.

Various applications of ionic tracers have been described in the literature. Common salt was used by Adolph Thiem and other German hydrologists as early as 1889 to determine the flow rate of ground water in sandstone and other media. Similar methods used for Cl^- were also postulated for ions such as nitrate (NO_3^-), dichromate (Cr_2O_7), and ammonium (NH_4^+) (Haas, 1959). Murray (1981) used lithium bromide (LiBr) in carbonate terrain to establish hydraulic connection between a landfill and a fresh-water spring where use of rhodamine WT dye tracer proved inappropriate. Sodium chloride (NaCl) was used by Mather (1969) to investigate the influence of mining subsidence on the pattern of ground-water flow. Tennyson (1980) used bromide (Br^-) to evaluate pathways and transit time of recharge through soil at a proposed sewage effluent irrigation site. Chloride (Cl^-) and calcium (Ca^+) were used by Grisak (1979) to study solute transport mechanisms in fractures. Potassium (K^+) was used to determine leachate migration and extent of dilution by receiving waters located by a waste disposal site (Ellis, 1979).

- Field Methods

The field techniques and required equipment for use of ion tracers are fairly simple and standard for all of the ionic elements in this group. It is primarily in the detection and analysis phases of a field study that techniques and required analytical equipment vary substantially. The basic equipment necessary to conduct a multiple-well fluid tracer test would include an injection well, observation wells or piezometric nest, auger (manual or power), well-casing driver (manual or power), steel measuring tape, tracer mixing and injection container, hand pump or automatic sampler, sample bottles, and break-through detection equipment (i.e., electrical conductivity/resistivity meter). Tests may be run utilizing a single borehole for injection and observation (Saleem, 1971) as discussed below, or by utilizing only one observation well given that the flow direction is established. Variations from the standard multiple-well test require modifications in equipment and techniques. The monitoring network (well configuration), sampling instrumentation, sampling frequency, and detection methods are dependent on the flow velocity and direction of the measured system. This information can be obtained using a conservative ionic tracer with a multi-observation well configuration. Knowledge of the ground-water direction and flow velocity is critical when conducting a single-well or two-well tracer study.

Several types of tracer tests have been performed successfully with ionic tracers, including two-well recirculating tests; radial flow tests; convergent flow slug tests; point dilution tests; and packer tests.

The concentration of ion to be injected should be such that it can be detected well above the natural background concentration level that exists in the receiving water. Density effects should be considered when determining injection concentration. One method to offset density effects is to raise the temperature of the injection mixture above that of the receiving ground water. Tracer dilutions of as much as six or seven orders of magnitude or greater may be unavoidable in field tracer tests (Thompson, 1980). The ion injection concentration should thus be high enough to ensure detectable levels (based on analytical techniques) in the observation well(s).

The ion tracer may be introduced as a powdered salt and allowed to dissolve in solution in the injection borehole. This passive injection technique results in negligible disturbance of the normal ground-water flow velocity and direction. This would be employed when the flow velocity is large or the distance between the injection well and the observation well is short. The ion tracer may also be introduced at a known flow rate and constant concentration. This technique would be a forced injection with a constant injection flow rate. This is useful in situations where the groundwater flow velocity (average pore velocity) is small and/or the distance between the injection and observation wells is large. The tracer may either be injected as a slug or as a continuous source input.

The simplest ion tracer tests do not require the collection of samples from the observation well. The technique developed by Slichter (1902) measures tracer recovery by changes in electrical conductivity of the ground water, and thus does not require further laboratory analysis. Sampling is required for other detection techniques (outlined in the following section), which are employed when density effects are significant and the injected ion concentrations are very low. There are two types of sampling: constant depth sampling and multi-level sampling. Sampling may be conducted manually using a hand pump or automatically using an electric or battery-operated sampler.

Lee (1980) employed a multi-level sampler to obtain pore water from various depths in a flow field. The sampler is a vertical bundle of polypropylene tubes which terminate in a small patch of nylon screen and are set at selected depths. The multi-level sampler is described as an effective and relatively inexpensive means of defining the spatial distribution and temporal variations of the tracer zone.

The number of samples kept for laboratory analysis can be minimized by making field measurements of electrical conductance within, ahead of, and behind the tracer slug (Lee, 1980). This field measurement provides an idea of relative breakthrough, and thus indicates when sampling frequency should be increased or decreased. When using samplers, each tube should be flushed before taking a sample by withdrawing and discarding one pump and tube volume.

- Detection and Analysis

As mentioned previously, the simplest and most inexpensive detection and analysis technique for ionic tracers is the measurement of electrical conductance as described by Slichter (1902). Electrical conductance can be used (as a break-through indicator) in two-well or multi-well tracer tests. The movement of an ionic tracer from the injection well towards the observation well is observed by means of an electric circuit that utilizes the conductivity of the ground water. As the tracer moves towards the observation well, the conductivity increases. An electric circuit within each observation well is used for detecting the time of arrival (break-through time) of the tracer (Haas, 1959).

Additional detection and analysis techniques are used if ionic tracers are injected at low concentrations, when greater accuracy is required, or in aquifer systems where electrical conductance is difficult to measure. The numerous detection and analytical techniques require that samples be collected in the field and that analyses be performed in the laboratory. The techniques applicable to specific ions are presented in Table 4.3. Several common techniques include specific ion electrodes, "Hach kit" analysis, liquid chromatography, gas chromatography, and mass spectrometry. Appendix E provides a further discussion of analytical methods for detection of tracers.

TABLE 4.3

Analytical Methods for Ionic Tracers

Ion	Method	Reference
Li^+, K^+	Atomic absorption	Brown et al. (1970)
Mn^{++}, Mg^{++}, Ni^{++}	Spectrophotometry	
K^+, Na^+	Flame emission Spectrophotometry	Pickett (1969)
Cl^-	Coulometric filtration Mercuric thiosulfate method	Cotlove (1964) Lee (1980)
$SO_4^=$	Turbidimetric	Hach (1969)
NH_4-N	U.V.-Visible spectrophotometry coupled with chemical procedures Brucine-sulfanilic acid Sulfanilamide-napthylenediamine Phenolhypochlorite-nitroprusside	" " USDI (1969a)
Br^-	Specific ion electrode Spectrophotometry Neutron activation	Tennyson (1980)

The overall costs of ionic tracer tests include both the cost of the injected ion (salt) and the costs of analysis. Common salts such as NaCl are relatively inexpensive, but some of the organic anions and fluorinated organic anions are expensive. With the exception of the electrical conductance, specific ion electrode, and Hach methods of analysis, the detection and analysis costs are significantly greater than the cost of the ionic compound. Cost is a limiting factor in the use of several detection methods. For example, Schmotzer et al. (1973) applied post-sampling neutron activation in a Br^- tracer test and pointed out that a major disadvantage with this technique is the significant cost of analysis. Each sample requires irradiation and generally chemical separation, counting, and quantitative analysis.

The concentrations of ionic solutions typically used in field tracer tests generally pose no measurable environmental or health effects. Water containing such concentrations of ions is much less palatable, but in most cases is potable. Schmotzer et al. (1973) reported that the only toxicity data on bromide (Br^-) was a result of medical research by Dreisback (1955) and Von Oettingon (1958). The report concluded that 50-100 mg of Br^-/100 ml of blood is the lower toxic limit for humans. For an adult, this limit is 2.4 grams of Br^- in the blood. A person drinking water with a bromide concentration of 200 ppm would have to drink 12 liters in order to ingest 2.4 grams of bromide. Natural background levels of bromide in ground water are usually low, and therefore low concentrations are typically employed in tests.

- Discussion of Specific Ion Tracers

Chloride (Cl^-): Background levels in ground water are typically moderate to high. Chloride can be used satisfactorily where density effects can be avoided and dispersion of clays is not likely. A chloride front proceeds at a high velocity and exhibits little distortion, resulting in sharp elution curves (Kaufman, 1956). See Figure 4.6 for a comparison of chloride, dextrose, fluorescein, and ^{131}I. The problem with chloride is the necessity of using high doses of NaCl to provide detectable concentrations at distant wells, and the danger of altering the permeabilities of high-clay soils by ion exchange. Kurty (1972) found that Cl^- and nitrate (NO_3^-) move at equal rates. Davis et al. (1980) reported that the injection concentration of NaCl should not exceed 3,000 mg/l (ppm) because of the increased density effects. Cl^- is a fairly conservative tracer which may be weakly adsorbed by some soils.

Bromide (Br^-): Bromide has low background levels in ground water, thus allowing low injection concentrations relative to chloride. Br^- is perhaps the most commonly used ion tracer. Jester and Uhler (1974) concluded that bromide was superior to chloride, iodide, fluoride, and vanadium when used as a tracer in soil-water systems with post-sampling neutron activation analysis. Schmotzer et al. (1973) reported that Br^- is biologically stable, and appears not to be lost by precipitation, absorption, or adsorption. Smith and Davies (1974) found that NO_3^- lags behind Br^- as a tracer. Expected background concentration of bromide will be <1 mg/l in most aquifers containing potable water (Davis et al., 1980). There are numerous techniques for detection and analysis of bromide, ranging from inexpensive methods (electrical conductance or specific ion electrode) to more expensive methods (neutron activation analysis or liquid chromatography).

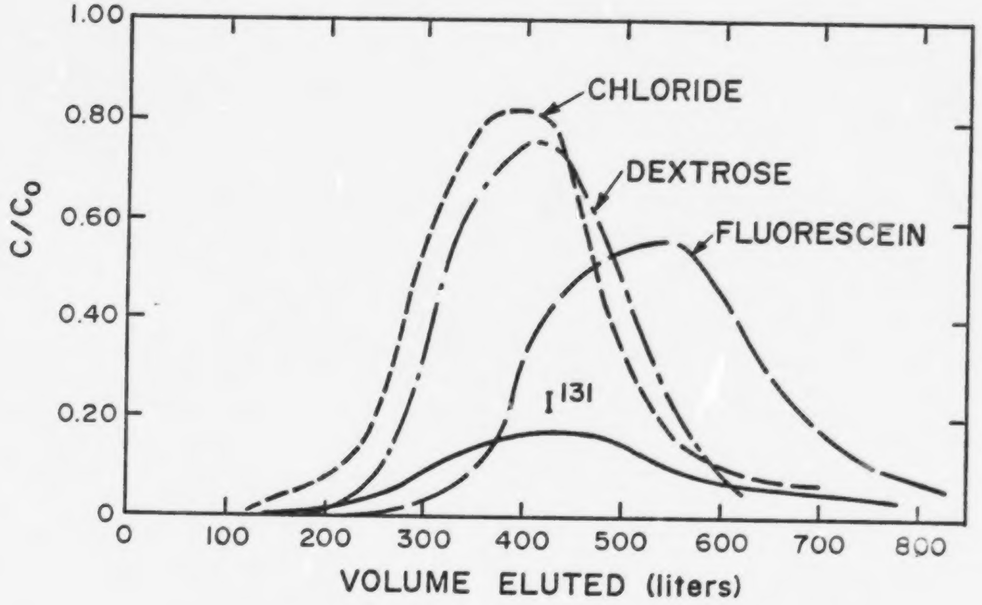


Figure 4.6. A comparison of several tracers in a laboratory test. Note that chloride shows less of an effect of sorption than the other tracers (figure adapted from Kaufman, 1956).

Lithium (Li^+): Lithium has a low (0.05 to 0.3 mg/l) background concentration in potable ground water, but has a high loss to ion exchange (Haas, 1959).

Ammonium (NH_4^+): This ion exhibits relatively high loss to ion exchange and the analysis of ammonia is more difficult than most other common ions (Haas, 1959). Natural background values in most potable water are below 5 mg/l.

Magnesium (Mg^{++}): As is true with other positive ions, Mg^{++} is subject to sorption and ion exchange. However, analyses are simple and inexpensive. Natural background values are commonly between 2 and 40 mg/l in potable ground water.

Potassium (K^+): A simple potassium ion will be sorbed and concentrations in water will be modified by ion exchange. Analyses are rapid and simple with atomic absorption or emission techniques. Expected background values in potable ground water are relatively low, ranging from about 0.2 to 10 mg/l.

Iodide (I^-): Iodide has very low background concentrations (generally <0.01 mg/l). Methods for sensitive analysis of I^- are relatively simple. However, iodide tends to be sorbed to a greater extent than either Br^- or Cl^- (Davis et al., 1980) and it is affected by microbiological activity.

Organic anions: These compounds have very low background concentrations, are nonsorbed, nonvolatile, and are highly to moderately stable. High precision measurement techniques are available with a detection sensitivity of 50 ppt. One disadvantage is the high cost of these compounds, which include benzoate and m-TFMBA. Malcolm et al. (1980) found that these compounds are highly mobile and have a good sensitivity of detection and a high precision of measurement using liquid chromatography.

Dyes

Various organic dyes have been used for surface-water and ground-water tracing since the late 1800's. Dyes are relatively inexpensive, simple to use, and effective. The extensive use of fluorescent dyes for water tracing began around 1960. Fluorescent dyes are preferable to non-fluorescent varieties due to much better detectability. Some non-fluorescent dyes include Congo Red and Malachite Green, which have been used in conjunction with cotton strip detectors (Drew, 1968) or with visual detection, often in soil studies. This discussion will concentrate on fluorescent dyes, which are more suitable for ground-water studies.

The most commonly used tracer dyes to be discussed include fluorescein, pyranine, lissamine FF, rhodamine B, rhodamine WT, and sulfo rhodamine B. Photine CU and amino G acid, two optical brighteners, will also be mentioned.

Table 4.4 gives the dyes by color, lists alternative names, and provides spectra wavelengths and filter combinations for their analysis. Several dyes may be used in a single tracer test if the absorption and emission spectra do not overlap. For example, Smart and Laidlaw (1977) recommended a combination of lissamine FF, amino G acid, and rhodamine WT. In general, the spectra do overlap, particularly for dyes of the same color. Figure 4.7 illustrates the excitation and emission spectra of rhodamine WT.

Although fluorescent dyes exhibit many of the properties of an ideal tracer, a number of factors interfere with concentration measurement. Fluorescence is used to measure dye concentration, but it may vary with suspended sediment load, temperature, pH, $CaCO_3$ content, salinity, etc. Other variables which affect tracer test results are "quenching" (some emitted

TABLE 4.4

GENERIC AND ALTERNATIVE NAMES AND CHEMICAL STRUCTURE OF THE TRACER DYES

Name	Alternative Names	Maximum Excitation, nm	Maximum Emission, nm	Primary Filter	Mercury Line, nm	Secondary Filter
Blue Fluorescent Dyes						
Amino G acid	7-amino 1,3 napthalene disulphonic acid	355 (310)	445	7-37*	365	98**
Photine CU		345	435(455)			
Green Fluorescent Dyes						
Fluorescein	Fluorescein LT Uranine Sodium fluorescein	490	520	98**	436	55**
Lissamine FF	Lissamine yellow FF Brilliant sulpho flavine FF Brilliant acid yellow 8G	420	515			
Pyranine	Pyranine Conc. D & C green 8	455(405)	515			
Orange Fluorescent Dyes						
Rhodamine B		555	580	2x1-60*+61**	546	4-97+3-66*
Rhodamine WT		555	580			
Sulfo rhodamine B	Pontacyl brilliant pink B Lissamine red 4B Kiton rhodamine B Acid rhodamine B	565	590			

Figures in parentheses refer to secondary maxima. For all spectra, pH is 7.0.
* Corning filter.
** Kodak Wratten filter.

Source: Smart and Laidlaw (1977)

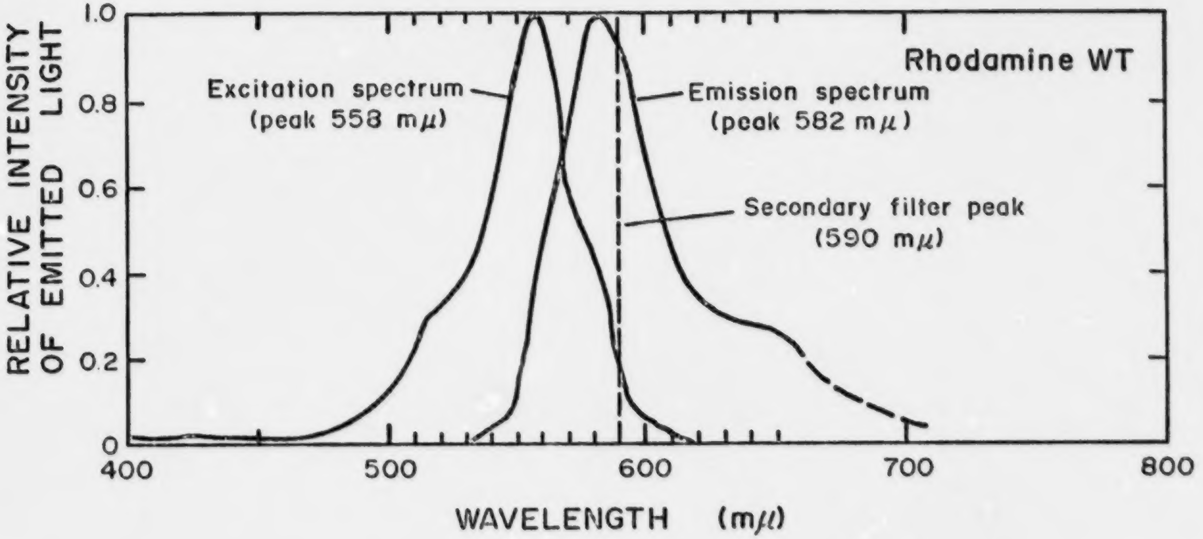


Figure 4.7. Excitation and emission characteristics of rhodamine WT, a fluorescent dye commonly used as a tracer (source, Wilson, 1968).

fluorescent light is reabsorbed by other molecules), adsorption, and photochemical and biological decay. These effects will be discussed in more detail in reference to specific dyes. Another disadvantage of fluorescent dyes is their poor performance in tropical climates, due to chemical reactions with dissolved carbon dioxide.

The advantages of using these dyes include their very high detectability, rapid field analysis, and relatively low cost and low toxicity. The theory of fluorescence is described by McLaughlin (1982) and Skoog and West (1980). As described by McLaughlin, the process of fluorescence involves the following steps: (1) energy is absorbed by the molecule from sunlight or an ultraviolet lamp and a transition to a higher, excited electron state takes place; (2) the molecule relaxes from the highest to the lowest vibrational energy of that state, losing energy in the process; and (3) if the excess energy is not further dissipated by collisions with other molecules (quenching), the electron returns to the lower ground electron state. This emission of energy due to the transition from the higher to the lower state is fluorescence.

• Field Methods

The basic equipment necessary for dye tracing is a manual or automatic sampler and a field or laboratory detection device. Sampling is performed by adsorption of dye onto packets of activated charcoal suspended in the water (in karst topography), or by taking grab samples at a discharge point (for karst, porous media or fractured rock studies). A filter fluorometer or a spectrofluorometer is generally used for analysis, although visual detection is sometimes used for qualitative results.

The tracer is introduced at a sink hole or well. The detection limit for fluorescent dyes is very low, so the quantity of tracer used is is relatively small. The amount of tracer needed has been approximated for karst systems by Drew and Smith (1969). They recommended using 60 grams of dye per kilometer of underground travel, per 0.15 cubic meters per second of discharge, at the largest likely rising. Atkinson et al. (1973) also described a method to calculate dye injection quantities for karst tests.

One sampling technique used in karst tracing is the Dunn method, developed in 1957. Small packets of fine mesh nylon or window screen are filled with activated charcoal and suspended in the watercourse at the sampling point. The dye adsorbs very strongly onto the charcoal, and is later eluted by placing the bag in a solution of 5% NH_3OH and ethyl alcohol. After soaking for one hour, the dye can be analyzed. The charcoal packets must be changed periodically, depending on flow rates and dilution of the tracer. Some examples of the use of this method are given in Gann and Harvey (1975) and Drew and Smith (1969). Cotton strip detectors have been used in a similar manner. Marston and Schofield (1962) described a tracer test using rhodamine B and cotton detectors.

Flow-through fluorimeters are sometimes used, which eliminate the need for sample collection. However, the most common method is collection of samples in sample bottles. Automatic samplers have been discussed in Chapter 3. Glass bottles should be used rather than polyethylene to avoid adsorption (Hubbard et al., 1982). Reznek et al. (1979) described procedures for sampling and analyzing fluorescein, and many of the procedures apply to other dyes. The samples and standards should be buffered to within a 5 to 11 pH range before analysis. If the samples are turbid, it is preferable to centrifuge the samples rather than filter them, as dye adsorbs onto the filter. The dye to be injected and the samples should both be stored out of sunlight and preferably in light-proof containers. Feuerstein and Selleck (1963) found that some fluorescent dyes exhibit a 50% photochemical decay in two days, even when stored in light-proof flasks. Obviously, it is advisable to analyze samples as soon as possible after sampling.

- Detection and Analysis

It is possible to visually detect some dyes in water at a concentration of about 40 ppm (Corey, 1968). This concentration is much higher than 10 ppb, which is the maximum permissible concentration allowed at drinking water intakes (Wilson, 1968). The visual detection method is qualitative and rarely used.

Other detectors are the filter fluorometer and the spectrofluorometer. The filter fluorometer (or fluorimeter) consists basically of an ultraviolet light source, glass curvets (sample holders), and sets of primary and secondary filters which correspond to the absorption and emission wavelengths of the dyes used. The filter fluorometer must be calibrated with standard solutions at the same temperature as the samples to be analyzed. As mentioned before, the fluorescence of a sample is affected not only by concentration of the dye, but also by background fluorescence, temperature, pH, turbidity, photochemical decay, and adsorption. Temperature control apparatus and correction charts are available, and methods to avoid the other interferences have been briefly discussed. Two U.S. Geological Survey publications are very useful for planning a fluorescent dye test and avoiding these interferences. "Fluorometric Procedures for Dye Tracing," by Wilson (1968) is a classic report, and in 1982, Hubbard et al. published a very useful updated report, "Measurement of Time of Travel and Dispersion in

Streams by Dye Tracing." These two are excellent references, as is the article by Smart and Laidlaw (1977).

Fluorometers are available with individual sample analysis capability, or with flow-through sampling (see Figure 4.8). They can be equipped with strip-chart recorders, and can be powered in the field with a portable generator (with a transformer) or a car battery (Hubbard et al., 1982). Some of the most well-known fluorometers are made by American Instrument Company and by G. K. Turner Associates.

Spectrofluorometers are more expensive and more complex to operate than filter fluorometers. They are generally not taken into the field. An example of this type of instrument is the Aminco-Bowman ultraviolet spectrophotofluorometer made by American Instrument Company. Table 4.5 shows sensitivity and minimum detection for certain dyes.

- Additional Information

The effects of temperature, pH, and suspended solids concentration on fluorescence have been mentioned. Fluorescence intensity is inversely proportional to temperature. Smart and Laidlaw (1977) described the numerical relationship and provide temperature correction curves. The effect of pH on rhodamine WT fluorescence is shown in Figure 4.9. An increase in the suspended sediment concentration generally causes a decrease in fluorescence. Adsorption on kaolinite caused a decrease in the measured fluorescence of several dyes, as measured by Smart and Laidlaw (see Figure 4.10).

The detected fluorescence may decrease, as in this example, or actually increase due to adsorption. If dye is adsorbed onto suspended solids, and the fluorescence measurements are taken without separating the water samples from the sediment, the dye concentration is a measurement of sediment

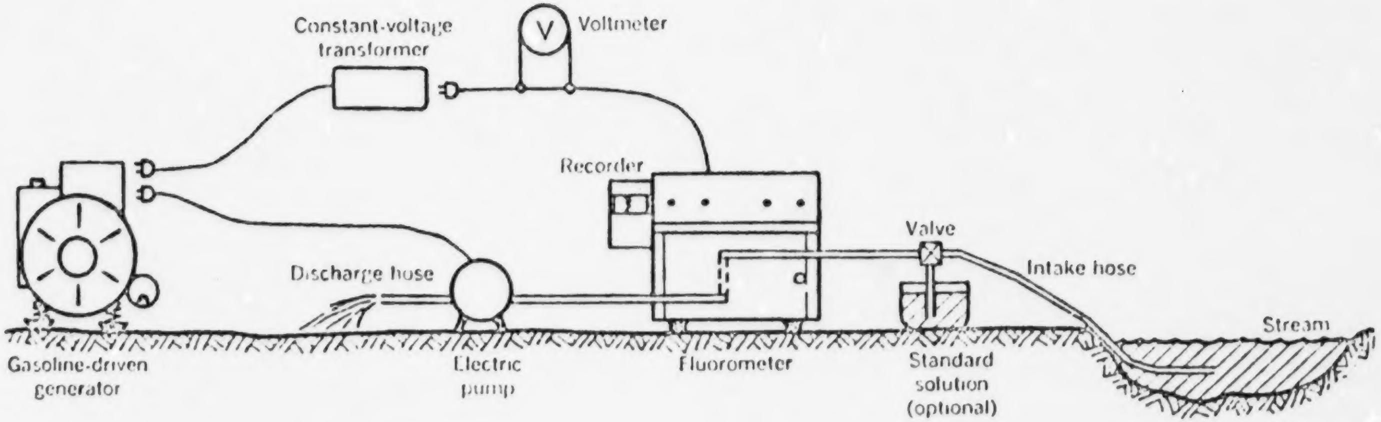

Constant-voltage transformer
Voltmeter
V
Recorder
Valve
Intake hose
Discharge hose
Stream
Gasoline-driven generator
Electric pump
Fluorometer
Standard solution (optional)

Figure 4.8. Cave streams or large springs can be monitored for dye tracers by using continuously recording fluorometers as shown schematically in this diagram by Wilson (1968). Less expensive but also less precise methods of monitoring for dye can use packets of activated charcoal which are placed in the stream. The dye, if present, is strongly sorbed on the charcoal which is then taken into the laboratory for analysis. The charcoal packets are replaced periodically in the stream until the test is finished.

Reproduced from best available copy.

TABLE 4.5

Sensitivity and Minimum Detectable Concentrations for the Tracer Dyes

Dye	Sensitivity* µg/l Per Scale Unit	Background Reading** Scale Units 0-100	Minimum Detectability*** µg/l
Amino G Acid	0.27	19.0	0.51
Photine CU	0.19	19.0	0.36
Fluorescein	0.11	26.5	0.29
Lissamine FF	0.11	26.5	0.29
Pyranine	0.033	26.5	0.087
Rhodamine B	0.010	1.5	0.010
Rhodamine WT	0.013	1.5	0.013
Sulfo rhodamine B	0.061	1.5	0.061

For a Turner 111 filter fluorometer with high-sensitivity door and recommended filters and lamp at 21°C.

* At a pH of 7.5.

** For distilled water.

*** For a 10% increase over background reading or 1 scale unit, whichever is larger.

Adapted from Smart and Laidlaw (1977).

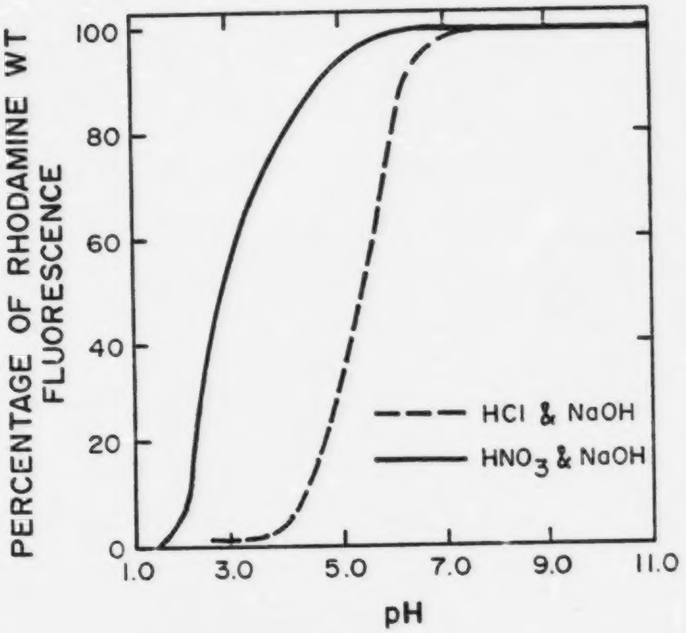


Figure 4.9. The fluorescence of most dyes is dependent on pH and the types of dominant ions present. Results of some experiments on the fluorescence of rhodamine WT are shown in this figure adapted from Smart and Laidlaw (1977).

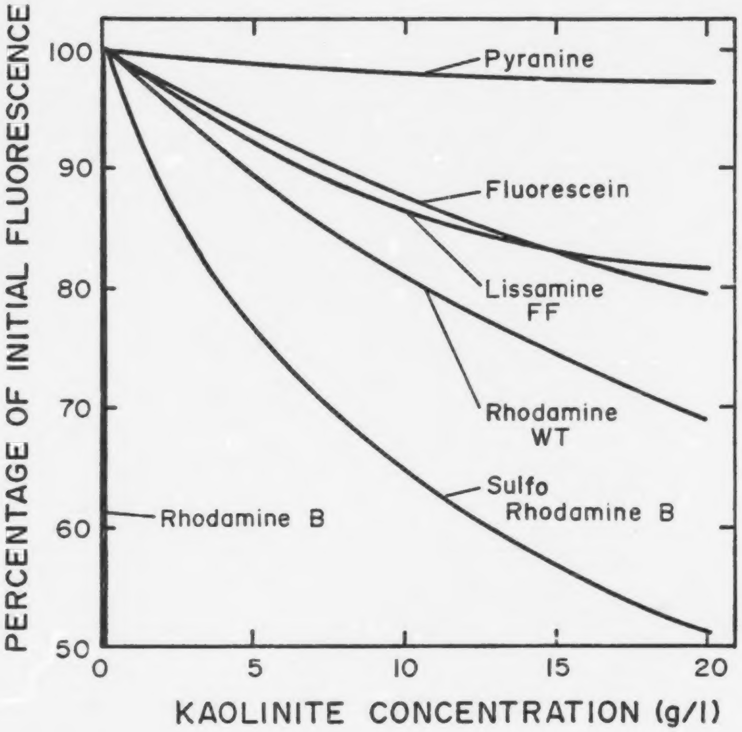


Figure 4.10. Most dyes will be adsorbed on fine particulate material, particularly on organic fragments and clays. Results of experiments with the adsorption of dyes on kaolinite (a type of clay) as reported by Smart and Laidlaw (1977) are shown in this illustration.

content and not of water flow. As mentioned before, the ideal separation is with a centrifuge, as the dye can adsorb onto filter paper. Adsorption can can occur on organic matter, clays (bentonite, kaolinite, etc.), sandstone, limestone, plants, plankton, and even glass sample bottles. These adsorption effects are a strong incentive to choose a non-sorptive dye for the type of medium tested.

Dyes travel slower than water due to adsorption, and are generally not as conservative as the ionic or radioactive tracers. See Figure 4.6 in the ion section for a comparison of chloride, dextrose, fluorescein, and I^{131}. Drew (1968) compared lycopodium, temperature, and fluorescein as karst tracers and found fluorescein breakthrough to be slowest (Figure 4.11). He questioned the ability of fluorescein to give accurate data on flow rates. Field data comparing the more recently developed dyes are not yet available. Atkinson et al. (1973) stated that an advantage of fluorescent dye measurement over lycopodium analysis is the ability to make deductions about discharges, changes in storage, and the geometry of the system. They suggest that dyes are more useful than spores for obtaining the maximum amount of quantitative information about a small karst system.

A final point concerning the interpretation of tracer tests is emphasized by Brown and Ford (1971). They obtained some very interesting results by running three identical dye tracer tests in the same karst system. These yielded three different flow-through times. One of the values differed by 50% from the original test value. Although only one test is generally run due to economic considerations, it may be advisable to run several tests to check reproducibility if accuracy is important.

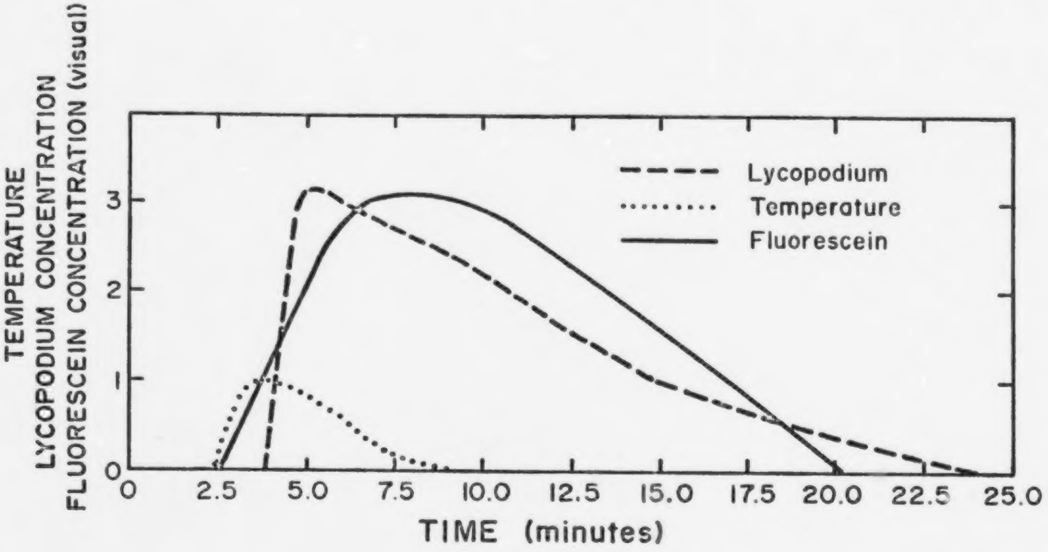


Figure 4.11. A comparison of the results of three simultaneous tracer tests in a karst system (data from Drew, 1968).

A comparison of the cost of various fluorescent dyes is given in Table 4.6. Prices are given in British pounds per kilogram for bulk dye. Volume labeled per unit cost is also listed, and rhodamine B appears to be the most cost effective. However, problems with its use will be discussed in a subsequent section.

Some of the available toxicity data will be mentioned in regard to specific dyes in the following section. Smart and Laidlaw (1977) discussed the toxicity of dye tracers, but regulations may change rapidly and should be researched before conducting a test. Current World Health Organization, Environmental Protection Agency, and state health standards should be consulted.

• Discussion of Specific Dye Tracers

Green Dyes

Fluorescein

Fluorescein, also known as uranin, sodium fluorescein, and pthalien, has been one of the most widely used dyes. Like all green dyes, its use is commonly complicated by high natural background fluorescence, which lowers sensitivity of analyses and makes interpretation of results more difficult. It has a very high photochemical decay rate compared to other dyes (Feuerstein and Selleck, 1963), but this is generally of little concern in ground-water tracing.

Feuerstein and Selleck (1963) recommended that fluorescein be restricted to short-term studies of only the highest quality water. Because this dye is affected strongly by pH (it becomes colorless in acidic conditions), they suggested that the sample pH be adjusted to greater than 6 before analysis. Fluorescein also exhibits an appreciable decrease in fluorescence with

TABLE 4.6

Relative Costs of Dyes

Dye	State	Relative Cost Per Kilogram*	Volume Labeled Per Kilogram** ($10^6 m^3/kg$)	Volume Labeled Per Unit Cost ($10^5 m^3/cost$)
Amino G Acid	powder	4	2	5.7
Photine CU	20% solution	1	3	6.0
Fluorescein	powder	4	4	10.0
Lissamine FF	powder	14	4	2.8
Pyranine	powder	13	12	9.2
Rhodamine B	powder	5	100	200.0
Rhodamine WT	20% solution	7	77	22.0
Sulfo rhodamine B	powder	9	16	17.8

After Smart and Laidlaw (1977).

* Costs are approximate and based on 1975 prices; the higher the number, the higher the price of the dye.

** Based on minimum detectabilities in Table 4.5.

increasing salinity, and is similarly affected by oxidizing agents and suspended solids (Reznek et al., 1979).

Some examples of fluorescein use include a fractured rock study by Lewis (1966). Borehole dilution tests resulted in hydraulic conductivity values similar to pump test values. Another example is a mining subsidence investigation in South Wales, where more than one ton of fluorescein was used in a sand-stone tracer test (Mather et al., 1969). A distance of 1,100 feet was traversed. Tester et al. (1982) used fluorescein to determine fracture volumes and diagnose flow behavior in a fractured granitic geothermal reservoir. He found no measurable adsorption or decomposition of the dye during the 24-hour exposures to rocks at 392°F. Omoti and Wild (1979) stated that fluorescein is one of the best tracers for soil studies, but Rahe et al. (1978) did not recover any injected dye in his hillslope studies, even at a distance of 2.5 meters downslope from the injection point. The same experiment used bacterial tracers successfully. Figure 4.11 compares fluorescein, lycopodium, and temperature as karst tracers.

An advantage of using fluorescein (or any of the green dyes) is its emission in the green band of the visible spectrum. Fluorescein can be visually detected at a concentration of about 40 ppm, but other means of detection are preferred since this is a relatively high concentration. The approximate sensitivity and minimum detection limit for fluorescein are given in Table 4.5.

Fluorescein is less costly in bulk than many of the dyes (see Table 4.6, but due to its high photochemical decay rate and high amount of adsorption, it increases in relative cost as the length of the test increases (more dye must be added to compensate for loss).

Pyranine

Another green fluorescent dye, pyranine, has a stronger fluorescent signal than does fluorescein, but is much more expensive. It has been used in several soil studies, and Reynolds (1966) found it to be the most stable dye used in an acidic, sandy soil. Omoti and Wild (1979) recommended pyranine and fluorescein as the best tracers for soil tests, although pyranine is relatively unstable if the organic matter content of the soil is high. Drew and Smith (1969) stated that pyranine is not as easily detectable as fluorescein, but is more resistant to decolorization and adsorption. Pyranine has a very high photochemical decay rate, and is strongly affected by pH in the range found in most natural waters (McLaughlin, 1982).

Lissamine FF

This green dye has been used primarily for aerosol tracing (Yates and Akisson, 1963), and hasn't been used extensively in ground-water tests. Little information is available on the performance of lissamine FF; however, Smart and Laidlaw (1977) recommended it as the best quantitative tracer of the three green dyes discussed. The dye is extremely stable and resistant to adsorption losses, but is much more expensive than most dyes.

Orange Dyes

Rhodamine B

Rhodamine B was the first of the three orange (or red) dyes to be used in water tracing. Its high adsorption losses make it a less suitable tracer for ground-water work than rhodamine WT or sulfo rhodamine B, although it has been used more frequently. Aulenbach et al. (1978) concluded that rhodamine B should not be used as a ground-water tracer due to sorption losses, and Feuerstein and Selleck (1963) reported significant adsorption. They also found that the fluorescence of rhodamine B is affected by large salinity changes. Knuttson (1968) reported that the dye is relatively unaffected by pH in the range found in most natural waters (5-10). The dye is sensitive to temperature (Omoti, 1977) and exhibits optical quenching by suspended solids. Like fluorescein, rhodamine B suffers from interference from high background fluorescence in tropical areas. It is less affected than the other rhodamine dyes by bacteria and light, but it adsorbs readily on bentonite, sand and gravel, till, and karst channels, pure quartz sand, and even plastic and glass laboratory columns (see Table 4.7). Hubbard et al. (1982) compared rhodamine B and rhodamine WT, and found high adsorption of rhodamine B on aquatic plants, suspended clays, and glass and plastic sample bottles. He found rhodamine WT easier to handle and more economical than rhodamine B. Although the unit cost of rhodamine B is lower, its loss rate is much higher than that of rhodamine WT.

Rhodamine B was decertified for use in cosmetics by the U.S. Food and Drug Administration in the 1960's. In 1968, it was illegal for use as a water tracer in the U.S. (Drew, 1968). Both rhodamine B and fluorescein were placed on toxicological classification C111 by the Food and Agriculture Organization/World Health Organization. Of the dyes discussed in this article, rhodamine B is generally recognized as the most toxic to man, as it is readily adsorbed on body tissue. Currently, the U.S. Geological Survey recommends that tracer tests should result in a final concentration less than 10μg/l. Numerous studies related to toxicity tests for various aquatic organisms are reported by Smart and Laidlaw (1977), and they recommend that the dye not be used as a water tracer.

Rhodamine WT

This dye has been considered one of the most useful tracers for quantitative studies, based on minimum detectability, photochemical and biological decay rates, and adsorption (Smart and Laidlaw, 1977; Wilson, 1968; and Knuttson, 1968). Hubbard et al. (1982) stated that it is the most conservative of dyes available for stream or karst tracing.

Some recent uses of rhodamine WT include projects by Burden (1981), Aulenbach et al. (1978), Brown and Ford (1971), Gann (1975), and Aulenbach and Clesceri (1980). Burden successfully used the dye in a water contamination study in New Zealand in an alluvial aquifer. Aulenbach and Clesceri also found rhodamine WT very successful in a sandy medium.

Gann (1975) used rhodamine WT for karst tracing in a limestone and dolomite system in Missouri. He used grab samples and activated charcoal packets, and traced a 14 km (8.7 mile) path. Three fluorescent dyes (rhodamine B, rhodamine WT, and fluorescein) were used by Brown and Ford (1971) in a karst test in the Maligne Basin in Canada. The highest recovery of dye (98%) was obtained for rhodamine WT. The fluorescein was not recovered at all. The horizontal flow path was 1.3 miles, and a Turner III fluorometer was used for analysis.

Aulenbach et al. (1978) compared rhodamine B, rhodamine WT, and tritium as tracers in a delta sand. The project involved tracing effluent from a sewage treatment plant. Sampling was performed with drive points, pumped wells, and lysimeters. The rhodamine B was highly adsorbed, while the rhodamine WT and tritium yielded similar break-through curves (see Figure 4.12). Rhodamine WT seems to be adsorbed less than rhodamine B or sulfo rhodamine B (see Table 4.7). Wilson (1971) found that in column and field studies, rhodamine WT did show sorptive tendencies.

Rhodamine WT is thought to be slightly less toxic than rhodamine B and sulfo rhodamine B (Smart and Laidlaw, 1977). This source notes that rhodamine WT and fluorescein are of comparable toxicity, but Aley and Fletcher

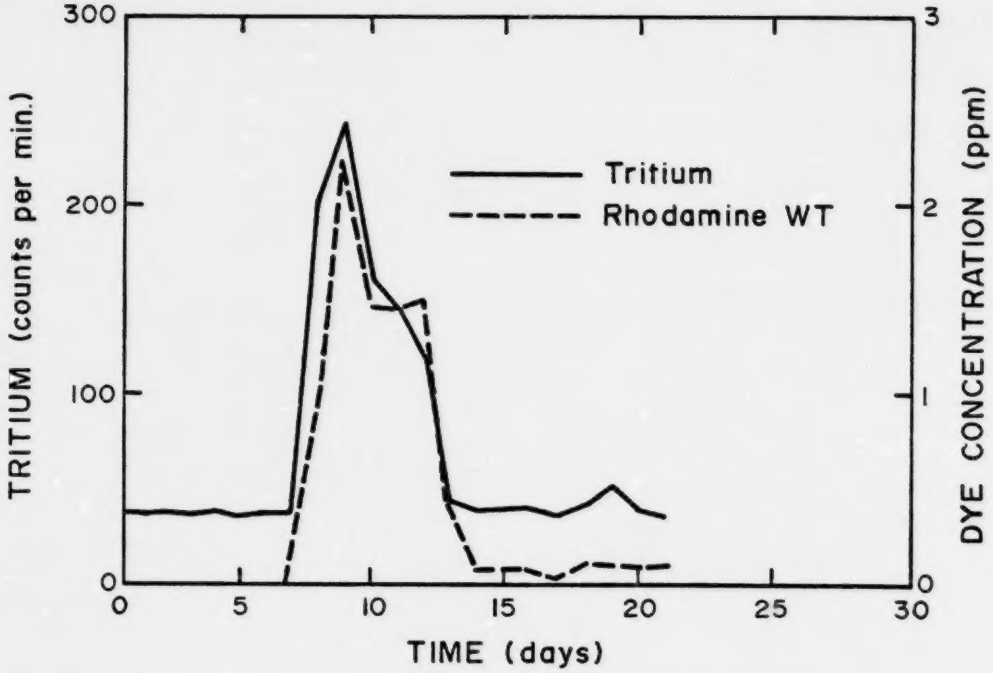


Figure 4.12. Although many researchers have found that rhodamine WT is sorbed on aquifer material, data presented by Aulenbach et al. (1978) suggest that this dye can be used in coarse, permeable sand. Comparative data from the study by Aulenbach et al. (1978) using tritium and rhodamine WT indicate little difference between the two tracers as shown in this figure adapted from their study.

TABLE 4.7

Measured Sorption of Dyes on Bentonite Clay

Dye	Losses Due to Adsorption on Clay
Rhodamine WT	28%
Rhodamine B	96%
Sulfo Rhodamine B	65%

Source: Repogle et al. (1966)

(1976) stated that rhodamine WT is not as "biologically safe" as fluorescein.

Sulfo rhodamine B

Sulfo rhodamine B, also known as pontacyl brilliant pink, has not been used extensively as a ground-water tracer. Its fluorescence is affected slightly by high salinity, and it exhibits low adsorption on suspended sediment (Feuerstein and Selleck, 1963). Table 4.7 compares the adsorption of the rhodamine dyes onto bentonite. This dye is more expensive than the other rhodamine dyes, and its toxicity appears to be slightly higher than that of rhodamine WT.

Blue Dyes

The optical brighteners are blue fluorescent dyes which have been used in increasing amounts in the past decade in textiles, paper, and other materials to enhance their white appearance. Water which has been contaminated by domestic waste can be used as a "natural" tracer, if it contains detectable amounts of the brighteners. Glover (1972) described the use of optical brighteners in karst environments. Examples of the brighteners are amino G acid and photine CU. These two are the least sensitive of the dyes reviewed (see Table 4.5), but the blue dyes have much lower background levels in uncontaminated water than do the green or orange dyes.

Photine CU is significantly affected by temperature variations, and both dyes are affected by pH below a pH of 6.0. The dyes have high photochemical decay rates, similar to those of pyranine and fluorescein. Amino G acid is fairly resistant to adsorption.

Toxicity studies on optical brighteners were reviewed by Akamatsu and Matsuo (1973). They concluded that the brighteners do not present any toxic hazard to man, even at excessive dosage levels.

Some Common Nonionized and Poorly Ionized Compounds

A number of chemical compounds will dissolve in water but will not ionize or will ionize only slightly under normal conditions of pH and Eh found in ground waters. Some of these compounds are relatively difficult to detect in small concentrations, others present a health hazard, and still others are present in moderate to large concentrations in natural waters thus making the background effects difficult to deal with in most settings. A list of a few of these compounds is given in Table 4.8.

The use of these and similar compounds as injected tracers in ground water is limited to rather special cases. Of those listed, boric acid would probably act most conservatively over long distances of ground-water flow. Boric acid has been used successfully as a tracer in a geothermal system (Downs et al., 1983). Large concentrations, 1,000 mg/l or more, would need to be used for injected tracers which, unfortunately, would pose difficult environmental questions if tracing were attempted in aquifers with potable water. From the standpoint of health concerns, sugars would be the most acceptable; however, they decompose rapidly in the subsurface and also tend to be sorbed on some materials. Results of an experiment using dextrose are shown in Figure 4.6. Alcohols such as ethanol would also tend to be sorbed on any solid organic matter which might be present. Another problem with the use of most of these compounds as tracers is that they would need to be introduced in moderately large concentrations which in turn would materially change the density and viscosity (particularly for glycerin) of the injected tracer mixture.

TABLE 4.8

A List of Some Simple Compounds Which are Soluble in Water

Name	Formula	Remarks
Silicic Acid	H_4SiO_4 (After combination with water)	Present in normal ground water in non-ionized form in concentrations of between 4 and 100 mg/ℓ. Low toxicity.
Boric Acid	H_3BO_3	Present in normal ground water in nonionized form in concentrations of 0.05 to 2.0 mg/ℓ. Toxic to plants above 1 to 5 mg/ℓ. Toxic to humans in higher concentrations.
Phosphoric Acid	H_3PO_4	Ionizes above pH of 6.0. Will form complexes with other dissolved constituents. Sorbs on or reacts with most aquifer materials. Natural concentrations mostly between 0.05 mg/ℓ and 0.5 mg/ℓ.
Acetic Acid	$C_2H_4O_2$	Moderately toxic in high concentrations. Water soluble. Natural concentrations are less than 0.1 mg/ℓ in ground water.
Ethyl Alcohol (Ethanol)	C_2H_6O	Major component of alcoholic drinks. Water soluble. Natural concentrations are less than 0.05 mg/ℓ in ground water.
Sugars		Major components of human and animal foods. Water soluble. Probably less than 0.2 mg/ℓ in most ground water.
Sucrose	$C_{12}H_{22}O_{11}$	
Maltose	$C_{12}H_{22}O_{11}$	
Lactose	$C_{12}H_{22}O_{11}$	
Glucose	$C_6H_{12}O_6$	
Glycerol (Glycerin)	$C_3H_6O_4$	Water soluble. Low toxicity. Probably absent in natural ground water.

Some of these compounds such as sugars, nevertheless, may be useful for simulating the movement of other compounds which are also subject to rapid decomposition but which are too hazardous to inject directly into aquifers.

Detection: Silica and phosphates can be determined by rather simple colorometric methods using standard solutions and photometric detectors. Boron is also detected by colorometric methods but the chemical procedure is more complicated than for silica and phosphate. The organic compounds listed in Table 4.8 are probably best detected by chromatographic methods. Also, high concentrations of glycerin and sugars are detected easily by optical refraction techniques.

Gases

Introduction: Numerous natural as well as artificially produced gases have been found in ground water. Some of these gases can serve as tracers which are already introduced, generally by natural processes, into the ground-water system. In addition, gas can be injected into ground water and the gas which is consequently dissolved can then serve as an injected tracer. Only a few examples of injected gases used for ground-water tracers are found in the literature.

The amount of gas which is dissolved in water increases with the gas pressure, decreases with an increase of temperature, and decreases with an increase of the salinity of the water. In most situations, once gas is dissolved in ground water at near-atmospheric pressures, the gas will tend to stay in solution as the water enters the ground-water system. This is due to the fact that fluid pressure increases rapidly as water moves downward into an aquifer and the gas will effectively be under a pressure far above the original pressure. If gas such as methane (CH_4) is being generated in the subsurface in large quantities, however, this gas may work its way as undissolved bubbles of gas through the aquifer and will remove much of the preexisting dissolved gases from the ground water.

Gases of potential use in hydrogeologic studies are listed in Table 4.9.

Inert Radioactive Gases: Chemically inert but radioactive ^{133}Xe and ^{85}Kr appear to be suitable for many injected tracer applications (Robertson, 1969; and Wagner, 1977) provided legal restrictions can be overcome. Of the natural inert radioactive gases, ^{222}Rn is the most abundant. It is one of the daughter products from the spontaneous fission of ^{238}U. Radon is present in the subsurface, but owing to the short half-life (3.8 days) of its principal isotope, ^{222}Rn, and the absence of parent uranium nuclides in the atmosphere, radon is virtually absent in surface water which has reached equilibrium with the atmosphere. Surveys of radon in surface streams and lakes have, therefore, been useful in detecting the locations of places where diffuse ground water enters surface waters (Rogers, 1958).

Inert Natural Gases: Because of their nonreactive and nontoxic nature, noble gases are potentially useful tracers. Helium is used widely as a tracer in industrial processes. It also has been used to a limited extent as a ground-water tracer (Carter et al., 1959). Neon, krypton, and xenon are other possible candidates for injected tracers because their natural concentrations are very low (Table 4.9). Although the gases do not undergo chemical reactions and do not participate in ion exchange, the heavier noble gases (krypton and xenon) do sorb to some extent on clay and organic material.

TABLE 4.9

Gases of Potential Interest as Tracers

Name of Gas	Approximate Natural Background Assuming Equilibrium with Atmosphere at 20°C (mg gas/liter water)	Maximum Amount in Solution Assuming 100% Gas at Pressure of 1 atm at 20°C (mg gas/liter water)
Argon	0.57	60.6
Neon	1.7×10^{-4}	9.5
Helium	8.2×10^{-6}	1.5
Krypton	2.7×10^{-4}	234
Xenon	5.7×10^{-5}	658
Carbon Monoxide	6.0×10^{-6}	28
Nitrous Oxide	3.3×10^{-4}	1100

The very low natural concentrations of noble gases in ground water make them useful as tracers, particularly in determining ground-water velocities in regional aquifers. The solubility of the noble gases decreases with an increase in temperature. The natural concentrations of these gases in ground water are, therefore, an indication of surface temperatures at the time of infiltration of the water. This fact has been used to reconstruct the past movement of water in several aquifers (Sugisaki, 1969; Mazor, 1972; Andrews and Lee, 1979).

Fluorocarbons: Numerous artificial gases have been manufactured during the past decade and several of these gases have been released in sufficient volumes to produce measurable concentrations in the atmosphere on a world-wide scale. One of the most interesting groups of these gases are the fluorocarbons (Table 4.10). The gases generally pose a very low biological hazard, they are generally stable for periods measured in years, they do not react chemically with other materials, they can be detected in very low concentrations, and they sorb only slightly on most minerals. They do sorb strongly, however, on organic matter.

Fluorocarbons have two primary applications. First, as an environmental tracer, they can be used in the same way tritium is used. Because large amounts of fluorocarbons were not released into the atmosphere until the late 1940's and early 1950's, the presence of fluorocarbons in ground water indicates that the water was in contact with the atmosphere within the past 30 to 40 years and that the ground water is very young (Thompson and Hayes, 1978). The second application of fluorocarbon compounds is for injected tracers (Thompson, Hayes, and Davis, 1974). Because detection limits are so low, large volumes of water can be labeled with the tracers at a rather

TABLE 4.10

Properties of Fluorocarbon Compounds

Common Name	Chemical Formula	Boiling Point at 1 atm (°C)	Solubility in Water at 25°C (weight %)
Freon-11	CCl_3F	23.8	0.11
Freon-12	CCl_2F_2	-29.8	0.028
Freon-113	$CCl_2F-CClF_2$	47.6	0.017
________	$CBrClF_2$	-4.0	unknown
________	CBr_2F_2	24.5	unknown
________	$C\ BrI-CBrF_2$	47.3	unknown

modest cost. Despite the problem of sorption on natural material and especially on organics (Figure 4.13), initial tests have been quite encouraging.

- Field Methods

Because the tracers are gases, it is most convenient to transport them to the field in pressurized containers for tracer injection. The gas is then bubbled into the water which is used for the tracer. For qualitative work, this is a simple task. If the initial tracer concentrations are to be established quantitatively, the gas injection should be made first into a container where the gas and injected water are turbently mixed and brought into equilibrium at a known temperature and pressure. Provision should be made to sample this labeled water just before it is injected into the aquifer to insure that the initial concentrations are constant during the test.

For most fluorocarbons, the tracers are dissolved first in the laboratory in methanol or some other solvent which is then injected as a liquid into the water which is used for the tracer test.

The most critical aspect of the field work is the sample collection and preservation. All gas tracers will be lost rapidly to the atmosphere unless samples are sealed in metal or glass containers. Most plastic containers are somewhat permeable to gas. Even certain types of glass are slightly permeable to light gases. Furthermore, all seals and caps should be metal or glass if fluorocarbons are being used because these compounds are sorbed strongly on many greases and plastic sealers.

The problem of the storage and shipping of water with fluorocarbon tracers is one of the major limitations of this method. Glenn Thompson, who has worked extensively with these tracers, has developed an analytical system for field use which largely eliminates the problem of sample integrity (Thompson and Hayes, 1978).

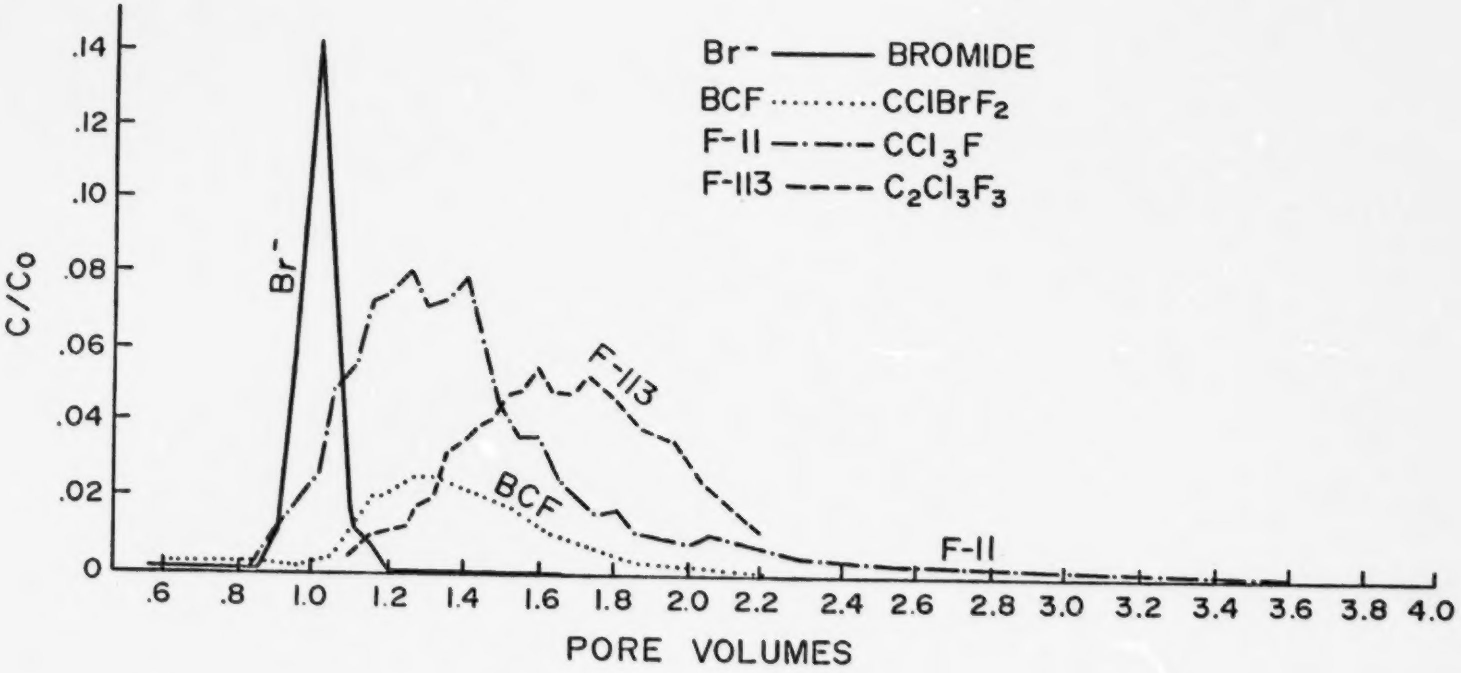


Figure 4.13(a). Laboratory experiments with fluorocarbon tracers and bromide flowing through a column of quartz sand. Note the reduced concentration peaks, the "tailing" of the curves, and the delay of the arrival of the peak concentrations relative to bromide caused primarily by sorption of the fluorocarbon tracers on the quartz (data from Thompson and Hayes, 1978).

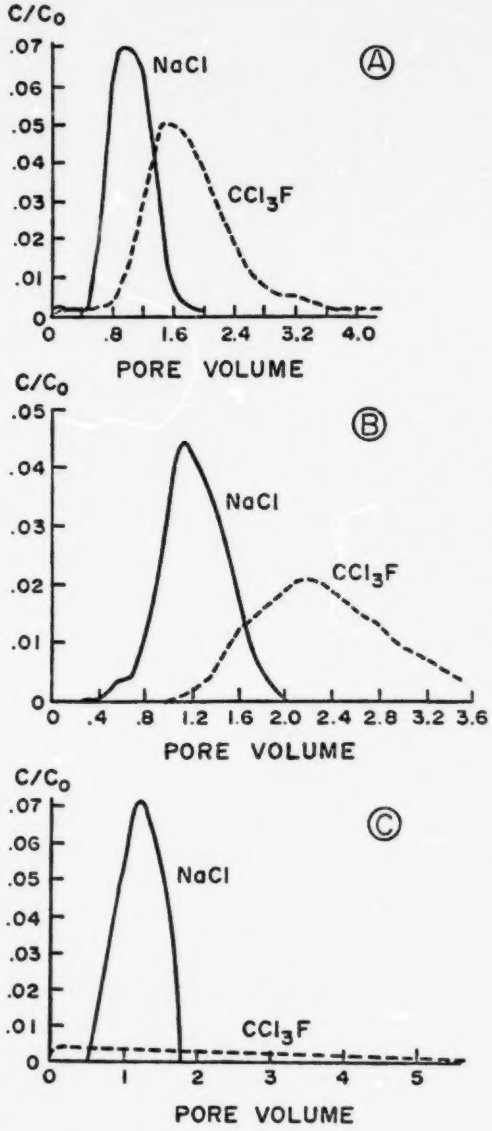


Figure 4.13(b). Tracer elution curves for laboratory experiments with NaCl (common salt) and CCl_3F (Freon-11 of trichlorofluoromethane) using (A) Ottowa sand (no fine material), (B) Yolo sandy loam (small amount of clay and some silt), and (C) crushed coal. Note that NaCl curves are similar for all experiments but that fine inorganic material reduces the peak concentration and delays the breakthrough curve for CCl_3F. Crushed coal, like most solid natural organic material, will adsorb most of the CCl_3F and will release it very slowly to the water as it passes through the test column. Data from Brown (1980).

- Analysis

Although a number of inexpensive gas-analysis kits are available, these are generally unsatisfactory for tracer studies. Quantitative analyses of gas should be done either with a gas chromatograph (GC) or a mass spectrometer (MS). Commonly a combined instrument, the GCMS, is used. The use of these analytical instruments is standard and within the training of all good analytical chemists. The difficult or nonstandard part of the analyses for most chemists, however, is in the method by which the tracer gases are removed quantitatively from the sample and fed into the analytical system. For most laboratories, the development of a gas stripping system for the samples is not a trivial task unless the chemists have had previous experience with the analysis of gas from water samples.

The measurement of fluorocarbon compounds is generally accomplished with an electron-capture detector used in conjunction with a gas chromatograph. Special care should be taken that no plastic connectors and valves are in contact with the sample being analyzed.

Stable Isotopes

Introduction: In this short section, we will look briefly at the use of natural stable isotopes for water tracers. A detailed treatment of the topic, however, is beyond the scope of this manual. The reader is referred to several excellent summaries of the topic (Gat, 1971; Fritz and Fontes, 1980; and Ferronsky and Palyakov, 1982).

An isotope is a variation of an element produced by differences in the number of neutrons in the nucleus of that element. Thus, hydrogen has two stable isotopes. One isotope (^1H) has only a proton and no neutron in the nucleus; the other (^{2}H) has a proton plus a neutron in the nucleus. In addition, hydrogen has an unstable, or radioactive, isotope (^{3}H) which has two neutrons in addition to the proton in the nucleus. An important characteristic of isotopes is that isotopes of an element, for all practical purposes, will react chemically in an identical way. For example, variations of sulfur isotopes (as ^{32}S, ^{34}S, and ^{36}S) in the sulfate ion will not affect the way in which the ion moves with the water. Thus, the water can be labeled with the isotope without affecting significantly the movement of the constituent.

In general, the uncertain ability to detect small artificial variations of most isotopes against the natural background, the high cost of their analysis, and the expense of preparing isotopically enriched tracers, means that stable isotopes are rarely used for artificially injected tracer studies in the field. They are, however, quite widely used to detect sources of pollution and to help determine areas of natural recharge.

Research into the topic of stable isotopes of various elements in natural waters is progressing rapidly, and the potential usefulness of these isotopes to ground-water tracing will undoubtedly increase markedly in the near future.

Hydrogen and Oxygen: The two stable isotopes of hydrogen (^{1}H and ^{2}H) and the three stable isotopes of oxygen (^{16}O, ^{17}O, and ^{18}O) form part of the water molecule, and analyses of their natural concentrations have been used widely to help understand the movement of ground waters. Natural variations in shallow ground water are generally related to variations within the original recharge water coming from the surface. Because of the large differences in mass between the two hydrogen isotopes, they tend to fractionate whenever evaporation or condensation of water takes place. Other factors being equal, waters with a higher ^{2}H (commonly called deuterium) content will be found near the coastlines, at low elevations, in warm rains, and in water which has undergone partial evaporation such as in soil moisture during periods of little rain or in saline lakes. Although mass differences among oxygen isotopes are not as large as those of hydrogen, natural fractionation of those isotopes also takes place. The variations in ^{18}O and ^{17}O contents of shallow ground water generally follow those of deuterium. That is, if the water has a larger than normal $^{2}H/^{1}H$ ratio, it will generally have also a larger than normal $^{18}O/^{16}O$ ratio (because ^{17}O is much less abundant than either ^{18}O or ^{16}O, it is rarely reported in routine isotopic studies). This general relationship is defined by Craig's line and is shown in Figure 4.14. Possible departures from this line can be caused by excessive evaporation, by reactions between minerals and hot water, and other less important effects.

The most common use of studies of ^{2}H and ^{18}O has been to trace the large-scale movement of ground-water and to locate areas of recharge (Figure 4.15).

Nitrogen: The two abundant isotopes of nitrogen (^{14}N and ^{15}N) can vary significantly in nature. Ammonia escaping as vapor from decomposing animal wastes, for example, will tend to remove the lighter (^{14}N) nitrogen and will leave behind a residue rich in heavy nitrogen. In contrast, many fertilizers with an ammonia base will be isotopically light. Natural soil nitrate will be somewhat between these two extremes. As a consequence, nitrogen isotopes have been useful in helping to determine the origin of unusually high amounts of nitrate in ground water.

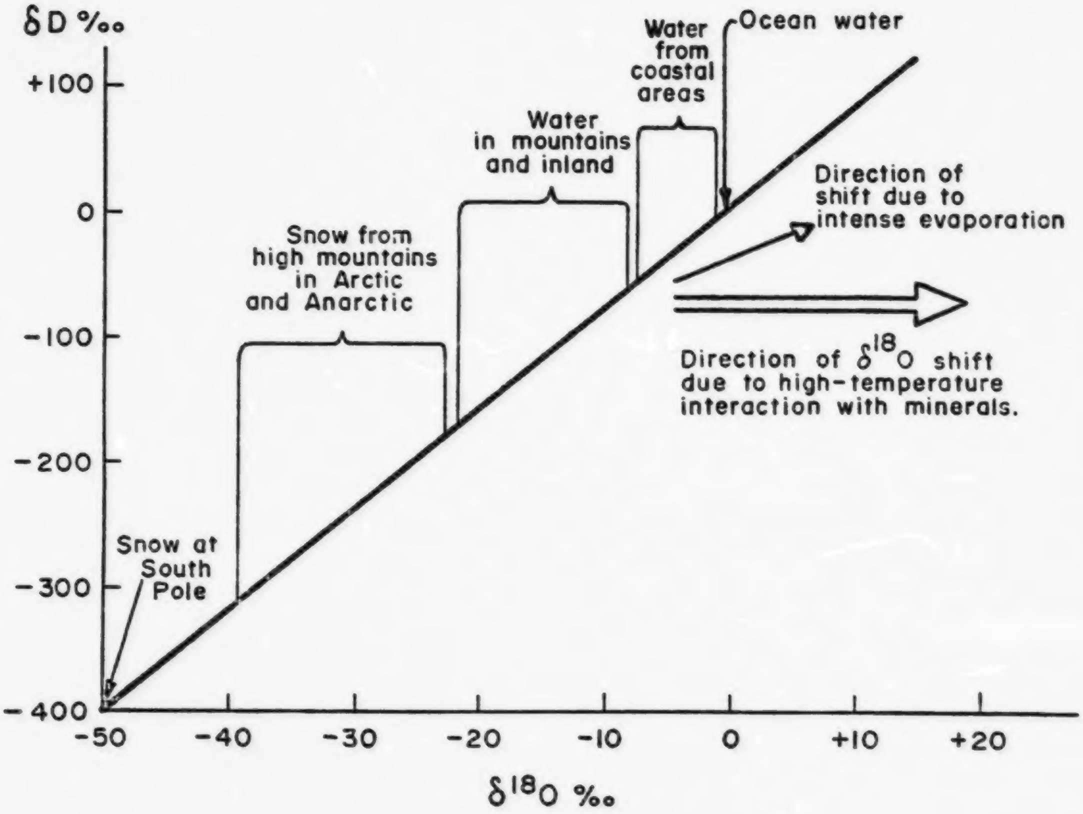


Figure 4.14. Relationship between deuterium and oxygen-18 for natural waters. Large arrow shows the direction of compositional change found in geothermal waters where heavy oxygen found in rock-forming minerals will exchange with the lighter oxygen in normal ground water (data from Ferronsky and Polyakov, 1982).

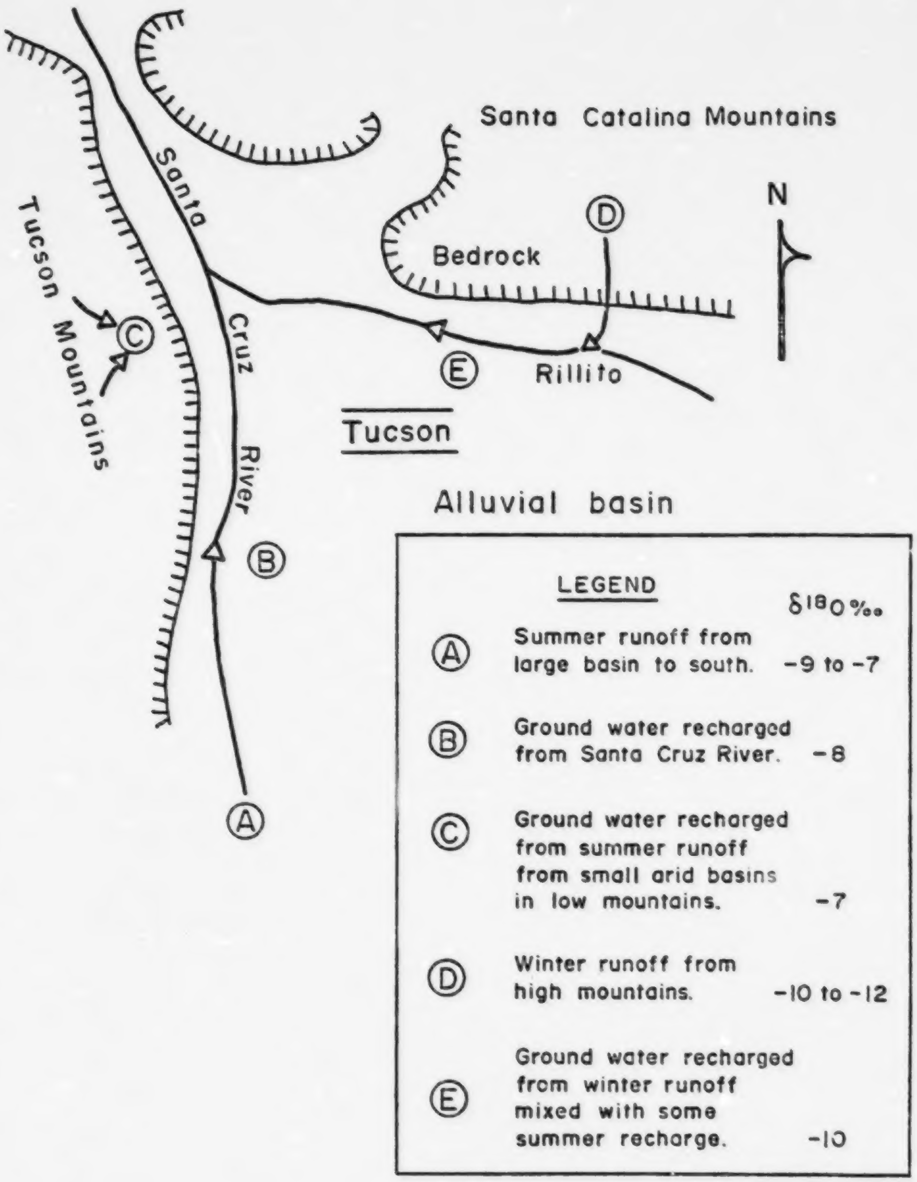

Santa Catalina Mountains
N
Bedrock
Ⓓ
Santa
Cruz
River
Tucson Mountains
Ⓒ
Ⓔ
Rillito
Tucson
Alluvial basin
Ⓑ
Ⓐ
LEGEND
δ18O‰
Ⓐ Summer runoff from large basin to south. -9 to -7
Ⓑ Ground water recharged from Santa Cruz River. -8
Ⓒ Ground water recharged from summer runoff from small arid basins in low mountains. -7
Ⓓ Winter runoff from high mountains. -10 to -12
Ⓔ Ground water recharged from winter runoff mixed with some summer recharge. -10

Figure 4.15. Differences in the stable isotope of oxygen (^{18}O) in ground water of the Tucson basin in Arizona reflect different sources of water. Because all values are negative, the larger number represents isotopically lighter water. Although the chemical characteristics of the ground water are quite similar throughout most of the basin, distinctive isotopic differences help to determine the origin of recharge for the basin. Data are from several unpublished M.S. theses at the University of Arizona. Diagram is not to scale.

Most nitrogen in ground water will be in the form of the nitrate anion (NO^-_3) or dissolved nitrogen gas (N_2) from the atmosphere. Locally in zones devoid of dissolved oxygen, the chemically reduced form (NH_4^+) may predominate. In general, nitrate will move as a conservative tracer and is an important indicator of pollution. If nitrate concentrations exceed about 10 mg/l, the health of infant mammals including humans may be adversely affected. Also, the presence of more than about 5 mg/l of nitrate commonly is an indirect indication of other forms of contamination including those from chemical fertilizers and sewage.

Sulfur: Most dissolved sulfur within shallow ground water is bound within the sulfate ion ($SO^=_4$). The stable sulfur isotopes (^{32}S, ^{34}S, and ^{36}S) found in the sulfate ion will vary quite widely and, under certain circumstances, be useful indicators of the origin of the sulfate. This is particularly true if, for example, one wishes to distinguish sulfate originating from natural dissolution of gypsum ($CaSO_4 \cdot 2H_2O$) from sulfate originating from an industrial spill of sulfuric acid (H_2SO_4).

Carbon: Two stable isotopes of carbon (^{12}C and ^{13}C) and one unstable isotope (^{14}C) are used in hydrogeologic studies. Most of the carbon dissolved in normal potable ground water is within the bicarbonate ion (HCO^-_3). Contaminated water may also have large amounts of organic materials which contain carbon. Other forms of carbon dissolved in natural water are carbonate ($CO^=_3$) and carbonic acid (H_2CO_3), the concentrations of which are pH-dependent, and the gases carbon dioxide (CO_2) and methane (CH_4).

Most isotopic studies of carbon in water have been centered on ^{14}C which will be discussed in a later portion of this chapter. Although not as commonly studied as ^{14}C, the ratio of the stable isotopes, $^{13}C/^{12}C$, are potentially useful in sorting out the origins of certain contaminants found in water. For example, methane (CH_4) originating from some deep geologic deposits is isotopically heavier than methane originating from near surface sources (Figure 4.16). This contrast forms the basis for identifying aquifers contaminated with methane from pipelines or from subsurface storage.

Isotopes of Other Elements: The potential exists for the use of stable isotopes of a number of other elements as natural tracers of water. Some of these are chlorine (^{37}Cl and ^{35}Cl), strontium (^{86}Sr and ^{87}Sr), boron (^{10}B and ^{11}B), and the isotopes of the noble gases. In general, studies of these isotopes are related more to the determination of regional directions of ground-water flow than to problems of the identification of sources of contamination.

- Field Methods

Collection of field samples must take into consideration problems of obtaining a representative sample as discussed in Chapter 3. Also, the sample must be preserved so that isotopic fractionation does not take place prior to analysis. For oxygen-deuterium samples, small glass bottles with vapor-proof caps which hold about 20 to 50 ml are sufficient for most purposes. For boron, nitrogen, carbon, and sulfur, a larger sample should be taken. The size of the sample will depend on the water chemistry and the analytical methods used. Generally, sample sizes are from 1 to 10 liters for normal potable water. Samples should be stored in the dark and a growth inhibitor should be added to water samples taken for boron, nitrogen, carbon, and sulfur analyses, because biological activity within the sample can cause significant isotopic fractionation. Analyses of stable chlorine will generally require samples of 1 to 2 liters of potable water and much less

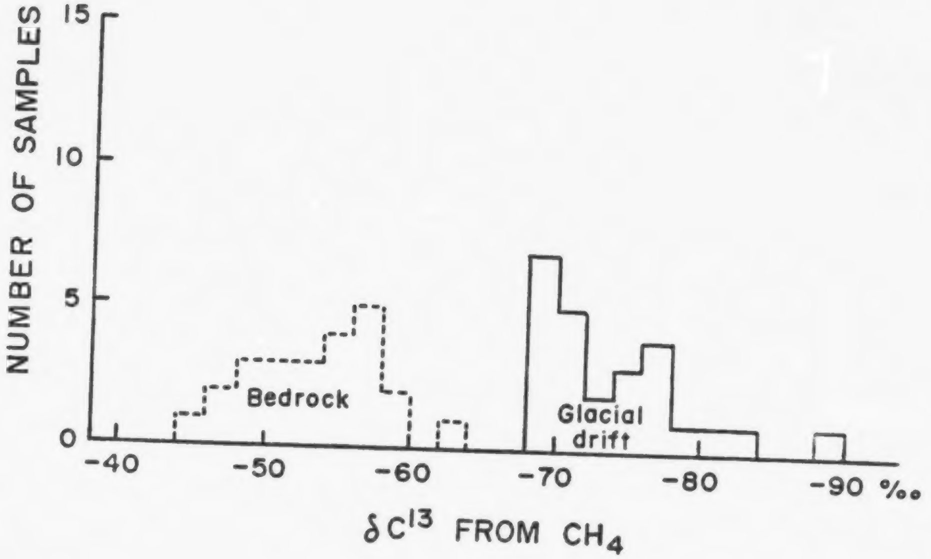


Figure 4.16. Histogram showing composition of carbon isotopes from methane from bedrock and from glacial drift. The contrast in isotopic composition allows the identification of methane from storage and from pipelines which may leak out and contaminate ground water. Natural methane generated in shallow aquifers is much different isotopically than bedrock methane that is distributed commercially. (Redrawn from Coleman et al., 1977).

for saline water. Changes in the isotopic ratios of chlorine will not take place under normal conditions of storage.

Analyses: Analyses of stable isotopes are made with expensive mass spectrometers which require highly-trained technicians to run. Further details are given in Appendix E.

Radionuclides

Introduction: This section includes a description of some of the hydrogeologic applications of radioactive isotopes of various elements, which are called collectively radionuclides.

In the early 1950's, great enthusiasm was evident for the use of radionuclides both as natural, "environmental" tracers and as injected artificial tracers. The environmental use has been expanded greatly until it is a major component of many hydrochemical studies of today. In contrast, the use of artificially injected radionuclides has all but ceased today in many countries including the United States. Most use of artificially introduced radioactive tracers in these countries is confined to carefully controlled laboratory experiments or to deep petroleum production zones which are devoid of potable water.

A brief explanation of some aspects of radioactivity is necessary before discussing isotopes of specific elements. Although for any radioactive element the radiation given off is in short, almost instantaneous, pulses which are randomly distributed in time, if enough individual nuclei are considered, the process of radioactive decay can be expressed as

$$\frac{dx}{dt} = - \lambda x \qquad (11)$$

in which x is the number of nuclei present, t is time, and λ is the decay constant which is unique to each radionuclide. If x_0 is the number of nuclei at zero time and x_t is the number of nuclei at time t, then

$$x_t = x_0 e^{-\lambda t} \tag{12}$$

The half-life of a particular radionuclide is the time which is taken for one-half the original number of nuclei to decay, or

$$t_{1/2} = \frac{\ell n\ 2}{\lambda} \tag{13}$$

The foregoing equations apply to all types of radioactive reactions even though some reactions produce alpha particles (^{4}He ions), others produce beta particles (electrons, both negatrons and positrons), and still others produce gamma rays (an electromagnetic radiation similar to X-rays). A number of other types of radiation may also be produced but they will not be discussed in this brief summary.

Injected tracers: For a number of reasons, the detection and counting of γ-radiation is much easier than either β or α radiation. Radionuclides which have a strong gamma emission are, therefore, commonly chosen for tracers. A number of these radionuclides as well as others are listed in Table 4.11. In addition, tracers are selected which can be injected into ground water in a form which is highly mobile in the water phase. This usually is either in a neutral or anionic form.

Most radioactive tracers are superior to other tracers because they can be detected easily by field equipment in very small concentrations which are far below levels that would alter the flow characteristics of the ground water. Also, tracers can be selected which have half-lives so short that they are essentially decayed after a few hours to a few days. Despite the demonstrated safety of many of the techniques and tracers, the complexity of

TABLE 4.11

Commonly Used Radioactive Tracers for Ground-Water Studies

Radionuclide	Radiation	Half-Life y=year, d=day, h=hour)	Chemical Compound
^{2}H	β^-	12.3y	H_2O
^{32}P	β^-	14.3d	Na_2HPO_4
^{51}Cr	γ	27.8d	EDTA-Cr and $CrCl_3$
^{60}Co	β^-, γ	5.25y	EDTA-Co and $K_3Co\ (CN_6)$
^{82}Br	β^-, γ	35.4h	NH_4Br, NaBr, LiBr
^{85}Kr	β^-, γ	10.7y	Kr (gas)
^{131}I	β^-, γ	8.1d	I and KI
^{198}Au	β^-, γ	2.7d	$AuCl_3$

local and federal regulations makes their field use impractical in many countries, including the United States.

Radioactive tracers, besides being used for tracers which move from one well to another, have been used for studies of the local hydraulics near and within a well. Radioactive gold (^{198}Au) when mixed with water in a well will plate out on the downstream side of the well as the water moves through the well. A directional counter will detect this concentrated radioactivity and thus indicate the direction of water movement in the vicinity of the well (Figure 4.17). Also, the rate of removal of the radioactivity from the well water will be a function of the volume of water moving through the well per unit time. Although giving only conditions near the well, this dilution technique is useful in obtaining estimates of hydraulic conductivity according to the following equations:

$$\frac{C_t}{C_o} = e^{-Bt} \qquad (14)$$

in which

C_t = concentration of tracer in the well of time t;

C_o = original concentration of tracer in the well at time = 0; and

B = a factor which is constant for simple, steady-state conditions.

If B is constant, then

$$B = \frac{Q}{V}$$

in which

Q = the volume of water per unit of time flowing through the well and V is the volume of water in the well.

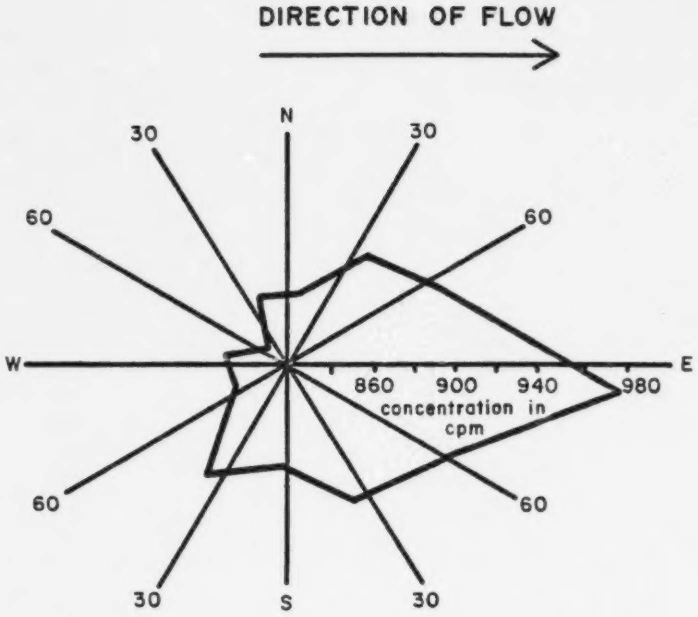


Figure 4.17. The local direction of ground-water movement as determined by the movement of a radioactive tracer within a borehole. The hole was not pumped during the test. The ground water is flowing under natural conditions and enters the well from the west and leaves the well towards the east. After release of the radioactive tracer, the gamma radiation is measured in different directions by rotating a shielded counter within the well. Although the surveys may be highly useful, it must be remembered that flow directions within the well are influenced by well-construction methods and by local heterogeneities in the aquifer. The measured directions, therefore, may not give a reliable indication of regional directions of ground-water flow. Diagram is redrawn from Rodriguez (1977).

For fully penetrating wells in isotropic and homogeneous aquifers,

$$Q = 2dmn_e\overline{v} \tag{15}$$

d = the effective diameter of the well;

m = the saturated thickness of the aquifer;

n_e = the effective porosity of the aquifer; and

$\overline{v}$ = the average velocity of the ground water outside of the well (in the aquifer).

If the hydraulic gradient, i, of the ground water is known, then the hydraulic conductivity, K, is given by

$$K = \frac{\overline{v}\ n_e}{i} \tag{16}$$

If the experiment has a duration which is 5% or more of the length of the half-life of the radioactive tracer, then Equation (12) should be used to correct for radioactive decay during the experiment. Thus in Equation (14), C_t is the calculated concentration at time t assuming no radioactive decay has taken place. It is not the actual observed concentration of radioactivity.

In summary, the progressive dilution of a tracer in a well can be used to obtain the hydraulic conductivity of an aquifer near the well provided dimensions of the well are known and estimates can be made of the effective porosity of the aquifer and the hydraulic gradient near the well.

Atmospherically Distributed Radionuclides: A number of radionuclides are present in the atmosphere from natural and artificial sources. Many of these radionuclides will be carried into the subsurface by rain water. The radionuclides of greatest interest are listed in Table 4.12. The most common

TABLE 4.12

Environmental Radionuclides

Radionuclide	Half-life (years)	Useful "age" range (years)	Comments
^{3}H	12.4	5-50	Analyses are done routinely at several laboratories. Useful for identifying young ground water in the subsurface.
^{14}C	5730	500-30,000	Analyses are done routinely in several laboratories. Sample collection and interpretation of results require experienced isotope hydrologist.
^{32}Si	103	50-100	Analyses difficult and done by only a few laboratories in the world. Interpretation of results is difficult.
^{36}Cl	3×10^{5}	5×10^{4}-2×10^{6}	Analyses done in only one or two laboratories in the world. Potentially an excellent radionuclide with which to study very old water. Also, sharp anthropogenic source in 1960's has produced a useful recent hydrologic tracer for ground water of recent origin.
^{39}Ar	269	100-1,000	Sample collection and analyses are extremely difficult. Has been utilized in Europe but new techniques are needed before the method can be applied widely.
^{85}Kr	10.7	3-30	Almost all ^{85}Kr is from anthropogenic sources. Sample collection and analyses are very difficult and have been done successfully only a few times. Potentially more useful than ^{3}H because increases in concentrations with time have been less erratic than increases of ^{3}H.

hydrogeologic use of these radionuclides is to obtain some estimate of the average length of time ground water has been isolated from the atmosphere. Because of dispersion in the aquifer and mixing in wells that sample several hydrologic zones, a unique age of the ground water does not exist. Nevertheless, it can be commonly established that most or virtually all the ground water is older than some given limiting value. In many situations we can say, based on atmospheric radionuclides, that the ground water was recharged more than 1,000 years ago or that, in another region, all the ground water in a given shallow aquifer is younger than 30 years.

Tritium, the radioactive isotope of hydrogen (^3H) with a 12.4-year half-life, was produced at low levels by natural processes prior to the detonation of thermonuclear devices in the early 1950's. Since that time, atmospheric tritium has been dominated by tritium from man-made sources. Most commonly, tritium concentrations are measured in tritium units (TU) which is the number of tritium nuclei per 10^{18} stable hydrogen nuclei. Prior to the 1950's, natural levels in rain ranged from 5 to 15 TU, the exact number depending on several local and regional factors. Owing to the decay of the tritium, water recharged during the early 1950's will only have 0.8 to 2.5 TU today if the water has been isolated from the atmosphere since that time. Thermonuclear explosions increased local rainfall to more than 1,000 TU in the Northern Hemipshere by the early 1960's (Figure 4.18). Tritium analyses of ground water are used widely to determine the "age" of young ground water. In general, ground water in the Northern Hemisphere which has more than about 5 TU is more than 30 years. Very small amounts, 0.05 to 0.5 TU, can be produced by natural subsurface processes, so the presence of these low levels

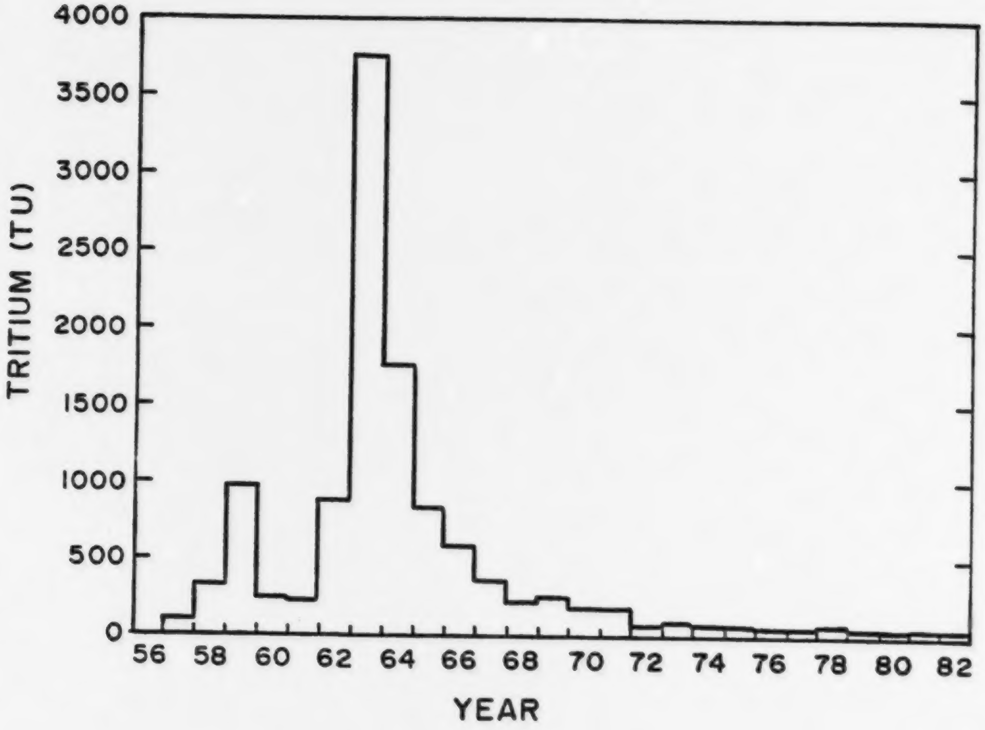


Figure 4.18. Average annual tritium concentration of rainfall and snow for the states of Arizona, Colorado, New Mexico, and Utah. During any single year, however, tritium concentrations may vary by more than 300% with the maximum concentrations in rainfall during the summer. In northcentral United States and central Canada, concentrations have been higher than those shown for the western states. Concentrations in precipitation along coastlines, in the tropics, and in the Southern Hemisphere are generally much lower than those shown here. (Diagram redrawn from Vuataz et al., 1984).

does not necessarily indicate water 40 to 60 years old or small amounts of more recent water mixed with very old water.

The radioactive isotope of carbon, ^{14}C, is also widely studied in ground water. Most ^{14}C in potable ground water is contained in the HCO_3^- ion in the water. Other carbon-bearing material dissolved in water such as CO_2, $CO_3^=$, CH_4, H_2CO_3, and organic acids may also contain variable amounts of ^{14}C. As a first approximation, the initial number of ^{14}C nuclei per total carbon nuclei, or X_0 in Equation (2), in a water sample is considered to have been constant due to the almost constant natural production of ^{14}C in the atmosphere by cosmic radiation interacting with the atmosphere. If the only source of ^{14}C in the water is originally from the active biosphere, then the ^{14}C which is measured in carbon from the water sample can be considered to be X_t in Equation (2). Because λ is known from experimental work, the "age" of the sample, or t, in Equation (2) can be determined directly.

In practice, however, the use of ^{14}C is rarely as simple as just described. Sources of old carbon, primarily from limestone and dolomite, will dilute the sample. A number of processes, such as the formation of CH_4 gas or the precipitation of carbonate minerals, will fractionate the isotopes and alter the apparent age. The complexity of the interpretation of ^{14}C "ages" of water is so great that it should be attempted only by hydrochemists specializing in isotope hydrology.

Despite the complicated nature of ^{14}C studies, they are highly useful in determining the approximate residence time of old water (500 to 30,000 years) in aquifers. For certain practical problems, this information is essential and cannot be obtained in any other way.

Other radionuclides listed in Table 4.12 are not used routinely in hydrogeologic work owing either to problems of sampling or to problems of analyses. Of those listed, ^{36}Cl will probably be used routinely in another decade after the present analytical bottleneck is solved. The major advantages of ^{36}Cl are the ease of sampling, the stability of the sample in storage, and the fact that ^{36}Cl can give information concerning extremely old water.

- Field Methods

Injected radioactive tracers are handled with great care to avoid radiation exposure and to avoid sample contamination. Otherwise, they are generally treated as normal chemical tracers. Special down-hole devices to measure in-place tracer dilution for the application of Equations (14), (15), and (16) are fabricated by the Institut fur Radiohydrometrie, Gesellschaft fur Strahlenund Umweltforschung MBH, Neuherberg, Ingolstadter Landstrasse 1, D-8042 Oberschleissheim, West Germany.

Field collection of samples for the determination of environmental levels of tritium must be done with great care to avoid contamination from the atmosphere, from local sources of tritium such as watch dials, and from high levels of tritium commonly present in laboratories. From two to four liters of water are needed if anticipated tritium levels are below 15 TU. Sample containers should be metal or high-quality glass. Some plastic containers are permeable to gases, so plastic containers are to be avoided unless the properties of the plastic are known.

Field collection of samples for ^{14}C is highly specialized and should be done by individuals experienced with this type of sampling. For routine ^{14}C samples, large volumes of water (from 10 to 1,000 liters) are required and the carbon is extracted either by large batch or by flow-through systems. The use of the tandem accelerator mass spectrometric (TAMS) method for ^{14}C analysis has greatly reduced the amount of carbon required so that one liter of water or less can be used. Access to the TAMS system, however, is not routine.

Samples for ^{36}Cl analyses are relatively simple to obtain. About 30 mg of chlorine should be available for the analysis. Most potable water contains between 10 and 100 mg/l of chloride, so a sample of a few liters of water generally is enough. Silver nitrate, $AgNO_3$, is mixed with the water sample, and AgCl is formed. The AgCl precipitate is placed in an amber bottle and stored out of sunlight and excessive heat until analyses can be completed.

- Analysis

The analysis of radioactive materials is a highly specialized branch of chemistry and is not easy to accomplish except where the field determination of gamma radiation can be related directly to the concentration of injected tracers. Scintillation counting using special liquid scintillation fluids is normally required for beta emitters.

Environmental radionuclides such as tritium, ^{14}C, and ^{36}Cl require very special equipment for their determination. Low-level tritium is concentrated by electrolysis and counted by liquid scintillation. A number of methods are used to determine ^{14}C. All processes are complicated. Many end with the carbon in a gaseous form which is placed into counters designed to receive gas. The TAMS method can be used for both ^{14}C and ^{36}Cl analyses. The accelerator used is a multi-million dollar instrument and only a few of these are presently in operation.

APPENDIX A

ADDITIONAL USES OF WATER TRACERS

The purpose of this manual is to describe ground-water tracing techniques. However, tracers are widely used in other areas of hydrologic study, such as surface water, the unsaturated (vadose) zone, and the atmosphere. Numerous engineering applications also involve tracer use, including petroleum exploration, leak detection, sewer flow, and biological and medical research. A brief description of these uses is given with reference articles.

Ground Water

Tracers have been used to determine the flow path, velocity, and residence time of solutes, and aquifer characteristics such as hydraulic conductivity, dispersivity, and effective porosity. Ground-water velocity and aquifer characterization studies have been described in the text.

Examples of flow path measurements are most numerous in karst studies. The Water Tracer's Cookbook (Aley and Fletcher, 1976), published by the Missouri Speleological Survey, is an excellent introduction to karst mapping and characterization through use of a wide variety of tracers. Another application of karst flow tracing is described by Gaspar and Oncescu (1972), and deals with water exchange between karst mines, depressed regions, and ground water. Karst tracing has also been used to delineate catchment boundaries (Smart, 1975). Flow path studies in non-karst regions include evaluation of the movement of sewage in ground water (Sinton, 1980), and the determination of the potential for chemical or bacterial pollution of a New

Zealand aquifer (Thorpe, 1979). Vecchioli et al. (1972) studied the travel of indicator bacteria through the Magothy aquifer in New York.

Residence time studies include the determination of ground-water recharge using environmental isotopes (Vogel et al., 1974, and Fontes and Fritz, 1975). Ground-water dating, involving the use of cosmic-ray and bomb-induced radioisotopes, is a growing field of study (Davis and Bentley, (1982). Environmental isotopes have recently been used to demonstrate the effect of ground water on storm runoff hydrographs (Sklash and Farvolden, 1979).

Surface Water

Tracers have been widely used in surface water studies to determine flow patterns (dispersion), flow volume, and time-of-travel (velocity). Kilpatrick et al. (1967) described flow measurements with fluorescent tracers. A more recent, general work on the subject is "Measurement of Time of Travel and Dispersion in Streams by Dye Tracing" (Hubbard et al., 1982), a handbook published by the U.S. Geological Survey.

Determination of flow patterns yields information concerning movement of contaminants (such as factory effluents, radioactive waste, and sewage) in streams (Gaspar and Oncescu, 1972). Study of dispersion under turbulent flow results in determination of eddy-diffusion coefficients. White (1981) discussed estuary mixing through the use of environmental radionuclides.

Gaspar and Oncescu (1972) reviewed the use of tracers in measuring flow rates in natural streams, closed conduits, and reservoirs. Dilution studies are used to find the time required for inflowing contaminants to be reduced to acceptable levels.

Storm runoff studies employ tracers to obtain travel time measurements in order to help establish flood hydrographs. Smith (1973) noted the use of environmental tritium in river recharge investigations.

Sediment transport is another aspect of surface water systems which has been studied with tracers. Elrick and Lawson (1969) looked at sediment movement in rivers, irrigation canals, estuaries, harbors, and the open ocean. River bank and bed erosion have also been investigated (Gaspar and Oncescu, 1972). White (1981) discussed the dating of sediments and surface water with environmental radionuclides.

Soil

In the unsaturated zone, soils have been investigated through the use of various tracers. Infiltration, drainage, and evapotranspiration are fields of interest. Recent research includes: the use of bromide as a tracer in the root zone of soils (Tennyson and Settergren, 1980); the use of radioactive tracers to determine the impact of deforestation on the soil profile (Ryckborst, 1981); and a general study of water distribution and movement in the unsaturated soil profile (Ligon, 1980).

Atmosphere

Environmental and injected tracers are utilized in estimating the travel of pollutants, studying precipitation and evaporation, and tracking air motion on a global scale through the use of nuclear debris (Elrick and Lawson, 1969).

Petroleum Industry

The oil and gas industry has developed tracers for a number of oilfield applications. Wagner (1977) described the use of chemical and radioactive tracers for waterfloods and gas drives in the tertiary oil recovery process. Some of the information to be obtained from diagnosis of interwell heterogeneities includes: identification of problem injection wells; directional flow trends and fluid velocity; and delineation of flow barriers. Preferred water and gas tracers are listed by Wagner (1977). Greenkorn (1962) also compared waterflood tracers.

Additional Engineering Applications

Leak detection in water and sewer pipes, embankments, and dams is another branch of tracer use (Gaspar and Oncescu, 1972). Zuber et al. (1979) discussed tracing of water leakage into salt mines, and Alburger (1977) described leak testing with dyes as a non-destructive technique for soils, sewers, electronics components, boilers, tanks, pipelines, etc. Koerner et al. (1979) reported non-destructive tracer testing methods for detecting dam seepage.

Sea-water intrusion around the foundation of a nuclear power plant was modeled by Myer (1981), using I^{131} as a tracer. Sewage system tracing has been performed by Renard (1982), and Aulenbach and Clesceri (1980) used tracers in monitoring the land application of waste water. Finally, sanitary landfill leachate has been traced by Ellis (1980) and Murray et al. (1981), using potassium (from the leachate) and injected lithium bromide, respectively.

Potential Uses

Radioactive, hazardous waste, and sanitary landfill disposal site evaluations are likely to employ tracer test results. In addition, soluble tracers can be mixed in dry form with wastes which are buried so that any water percolating later through the waste will carry the tracer which in turn could provide an early warning for the arrival of the bulk of the slower moving and hazardous leachate from the waste.

APPENDIX B

A DISCUSSION OF DISPERSION AND DIFFUSION

One of the purposes of many tracer tests is to obtain a value of the aquifer parameter, dispersivity (α). The intent of this Appendix is to discuss briefly the theoretical background of the parameter, and to present some current attitudes concerning dispersion.

The transport of a tracer or contaminant in a porous medium is analyzed by some form of the convection-dispersion equation, introduced by Ogata and Banks (1961), and discussed by Bear (1961a, 1969). Convection is the bulk movement of water at the mean velocity of the flow system, u (where u equals specific discharge divided by porosity, as defined in Chapter 2). Convection may be caused by differences in density of the water (natural convection), regional movement in the aquifer (advection), and the pumping of wells (forced convection) (Sauty, 1980).

Dispersion is the mechanism which causes a solute to mix and spread to positions which would not be expected by convection alone. Dispersion in ground water is a combination of mechanical dispersion (mixing) and molecular diffusion, and it causes a dilution of the solute. Mechanical dispersion is due to variations in fluid velocity, and the tortuous flow paths in the voids of the porous medium at the microscopic scale (Sudicky and Cherry, 1979). On a larger scale, mixing is due to the presence of zones of different permeabilities.

Molecular diffusion is caused by Brownian motion, and is often considered insignificant in magnitude in comparison with mechanical dispersion, for rapidly flowing ground water. In most tracer tests in porous media, diffusion is neglected because the rate of ground-water flow is too high for pore-to-pore equalization of concentration (Perkins and Johnson, 1963). A reasonable value for the diffusion coefficient for non-adsorbed species in porous media is 1×10^{-10} m^2/s (Freeze and Cherry, 1979), while the dispersion coefficient is generally orders of magnitude larger.

Derivation of the Convection-Dispersion Equation

The convection-dispersion equation used in contaminant transport modeling is based on Fick's first and second laws. Formulated by analogy to heat conduction, the first law states that the flux of a diffusion or dispersing substance in a given direction is directly proportional to the concentration gradient in that direction. The negative sign indicates that flux is positive in the direction of decreasing concentration. In the following text, dimensions are given in brackets.

$$F_x = - D_x \frac{\partial c}{\partial x};$$

where F_x = mass flux $[\frac{M}{L^2T}]$ in the x direction;

D = coefficient of proportionality $[\frac{L^2}{T}]$;

c = concentration $[\frac{M}{L^3}]$.

Fick's second law is derived from the law of conservation of mass, as applied to the first law. It states that:

$$\frac{\partial c}{\partial t} = D\nabla^2 c$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2}\,\hat{i} + \frac{\partial^2}{\partial y^2}\,\hat{j} + \frac{\partial^2}{\partial z^2}\,\hat{k}$

This assumes that D is constant, while it is actually a function of temperature, concentration, and other factors.

The convection-dispersion equation for a non-reactive solute is stated, in one-dimensional form, as:

$$\frac{\partial c}{\partial t} = -u\,\frac{\partial c}{\partial x} + D\,\frac{\partial^2}{\partial x^2}$$

where

D = coefficient of dispersion $[\frac{L^2}{T}]$;

u = average linear flow velocity.

This assumes that flow is parallel to the x direction, with steady-state velocity, u. It also assumes that the fluid is incompressible.

The coefficient of dispersion, D, may be thought of as a correction factor which describes the variation of solute distribution about the mean. The coefficient, D, is a combination of the effects of hydrodynamic dispersion and molecular diffusion.

$$D = \alpha_L u = D_M$$

Here, α_L = longitudinal dispersivity (in the x direction) [L];

D_M = molecular diffusion coefficient $[\frac{L^2}{T}]$.

The term "dispersivity" was introduced by Scheidegger (1954). This parameter has components in three orthogonal directions. The longitudinal dispersivity is in the direction of flux. Horizontal transverse dispersivity may be called "lateral dispersivity", and vertical transverse dispersivity may be referred to as "vertical dispersivity." In laboratory experiments, the transverse dispersivities are generally 5 to 20 times smaller in magnitude than the longitudinal dispersivity (Freeze and Cherry, 1979).

Solution of the Convection-Dispersion Equation

The one-dimensional solution of the convection-dispersion equation for a step-function input of tracer into a semi-infinite aquifer with natural flow velocity (Ogata and Banks, 1961) is:

$$c/c_0(x,t) = \frac{1}{2}\,[\text{erfc}\,(\frac{x-ut}{2Dt} + \exp\,(u_x/D)\ \text{erfc}\,(\frac{x+ut}{2Dt})] \qquad (21)$$

where

c/c_0 = normalized concentration (relative to source):
x = distance from the measuring point to the source;
u = average linear velocity;
t = time;
D = dispersion coefficient;
erfc = the complimentary error function.

The boundary conditions are:

$c(x<0,\ t) = 0$, for all t
$c(0,\ t) = C_0$, for all $t > 0$
$c(\infty,\ t) = 0$, for all t

The solution above can be approximated, after a short period of time, by:

$$c/c_0 = \frac{1}{2}\,\mathrm{erfc}\left[\frac{x-ut}{2Dt}\right] \tag{22}$$

This equation can be solved for various boundary conditions, flow regimes, and types of injection (e.g., uniform flow, radial flow, continuous injection, slug injection). Fried (1975) provided a number of solutions, and Sauty (1977) developed type curves for uniform or radial flow to characterize response to continuous or instantaneous pulse input at a point. Lenda and Zuber (1970) developed analytical solutions in normalized form for different measurement geometries. They presented type curves for point injection and line injection in an infinite aquifer. Sudicky and Cherry (1979) developed type curves for a finite-width pulse injection.

Hoopes and Hareleman (1967a) presented a general equation describing the nonsteady-state concentration of a tracer during plane radial flow. Analytical solutions to this equation for a constant input concentration have been given in that paper and by Gelhar and Collins (1971). These solutions can be used for single-well injection/withdrawal tests.

For a two-well tracer test, Webster et al. (1970) and Grove and Beetem (1971) provided solutions. The tracer addition can be continuous or a pulse, and recirculation can be accounted for.

Measuring Dispersivity

The error function is related to the normal distribution[1] ($\underline{O}$), as:

$$\underline{Q}\,(z) = \frac{1}{2}\left[1 + \mathrm{erfc}\left(\frac{z}{2}\right)\right] \tag{23}$$

---

[1] This holds for tables of the normal distribution with negative infinity as the lower limit.

Then,

$$c/c_0 = 1 - \underline{\theta}\left[\frac{x-ut}{2Dt}\right] \tag{24}$$

This states that the normalized concentration distribution can be described by a cumulative normal distribution with a mean of zero and a variance equal to 2Dt. The variance is also equal to $2\alpha_L\overline{x}$. This is true because $D = \alpha u$, and $\overline{x} = u \cdot \overline{t}$. Here, $\overline{x}$ and $\overline{t}$ are average distance and average time. Then, by plotting c/c_0 versus x on normal probability paper, the value of α_L is obtained.

The Scale Effect

It has generally been assumed in the past that dispersivity (α) is an aquifer property which is constant. In the past ten years, research has indicated that dispersivity is scale-dependent (Fried, 1975). Laboratory breakthrough curves in packed granular columns yield longitudinal dispersivity values of 0.01 to 1 cm (Pickens and Grisak, 1981). Values of α_L obtained by field tracer tests range from 1 to 134 meters (see Table 1), generally increasing with increasing distance between injection and observation wells. Dispersivity values have also been obtained by calibration of computer models. The longitudinal dispersivity values in Table B.1 range from 12 to 91 meters.

Several ideas have been offered to explain these results. Pickens and Grisak (1981) have suggested that field tracer tests which are analyzed using a one-dimensional flow field may produce a scale effect which is partially a consequence of streamline effects (converging or diverging streamlines).

TABLE B.1

VALUES OF DISPERSIVITIES MEASURED BY VARIOUS METHODS

Single-Well Injection Withdrawal Test

Type of Aquifer	Location	α_L (meters)	Reference
Alluvial	Lyons, France	0.1-0.5	Fried, 1975

Multiple-Well Tracer Test (including two-well tracer tests)

Type of Aquifer	Location	Distance Between Injection and Observation Wells (meters)	α_L (meters)	Reference
Chalk	Dorset, England	8	3,1	Ivanovich and Smith, 1978
Alluvial	Lyons, France	6 & 12	4.3	Fried, 1975
Alluvial	Eastern France	6 & 12	11.0	Fried, 1975
Fractured dolomite	Carlsbad, NM	55	38.0	Grove and Beetem, 1971
Fractured carbonate	So. Nevada	121	15.0	Classen and Cordes, 1975
Fractured crystalline	Savannah River Plant, S.C.	538	134.0	Webster et al., 1970

Single-Well Tracer Test with Surface Geophysics

Type of Aquifer	Location	Distance Traveled by Tracer (meters)	α_L (meters)	α_T (meters)	Reference
Alluvial	Lyons, France	~ 80 m	5-12	0.009-14.5	Fried, 197

TABLE B.1 (continued)

Dispersivities Measured on a Regional Scale By Model Calibration

Type of Aquifer	Location	Approximate Distance Traveled by Solute (meters)	α_L (meters)	α_T (meters)	Reference
Alluvial	Lyons, France	1,000	12	4	Fried, 1975
Limestone	Brunswick, GA	1,500	61	18	Bredehoeft & Pinder, 1973
Alluvial	Rocky Mtn. Arsenal, CO	4,000	30	30	Konikow, 1977
Alluvial	Arkansas River Valley, CO	5,000	30	9	Konikow & Bredehoeft, 1974
Glacial deposit	Long Island, NY	1,000	21.3	4.3	Pinder, 1973
Basalt	Snake River Plain, ID	4,000	91	137	Robertson, 1974

Pickens et al., (1976) suggested that large dispersivities obtained from analysis of two-well tracer tests are a result of mixing of water from different levels, which occurs at the well bore.

Most researchers feel that the primary cause of the scale effect is the heterogeneity of an aquifer (Warren and Skiba, 1964; Matheson and de Marsily, 1980; and Gelhar et al., 1979). Recent research indicates that, for certain hydraulic conductivity distributions, the longitudinal dispersivity approaches a constant at large time or large mean travel distance. Gelhar et al. (1979) suggested an improved form of the convective-dispersive transport equation which incorporates the statistical properties of the hydraulic conductivity distribution. However, the traditional convection-dispersion equation and its solutions continue to be used to obtain values of dispersivity until a better alternative is found.

APPENDIX C

FACTORS TO CONSIDER IN TRACER SELECTION

PURPOSE OF STUDY

		Tracer Type to be Used
Determination of:	flow path	
	velocity (solute)	Nonconservative
	velocity (water)	Conservative
	porosity	Conservative
	dispersion coefficient	Conservative
	distribution coefficient	Nonconservative
Delineation of contaminant plume		Constituent of plume
Recharge		Environmental isotope or anthropogenic compound
Dating		Radioactive isotopes

AVAILABLE FUNDS

Manpower and equipment to run tests to completion (e.g., drilling, tracer cost, sampling, analysis).

TYPE OF MEDIUM

	Tracer Type
Karst	Fluorescent dyes, spores, tritium, as well as other tracers
Porous media (alluvium, sandstone, soil)	Wide range of choices. Dyes and particulate material are rarely useful.
Fractured rock	Wide range of choices. Dyes and particulate only occasionally useful.

STABILITY OF TRACER

Distance from injection to sampling point	Must be stable for length of test and analysis
Approximate velocity of water and approximate estimate of time required for test, given: distance from injection to sampling point, porosity, thickness of aquifer	

DETECTABILITY OF TRACER

Background level

Dilution expected in test (function of distance, dispersion, porosity, and hydraulic conductivity)

Detection limit of tracer (ppm, ppb, ppt)

Interference due to other tracers, water chemistry

DIFFICULTY OF SAMPLING AND ANALYSIS

Factors to Consider	Example of Difficult Tracer
Availability of tracer	Radioactive (must have special permits)
Ease of sampling	Gases (will escape easily from poorly sealed container)
Availability of technology for and ease of analysis	Cl-36 (only one or two laboratories in the world can do analyses)

PHYSICAL/CHEMICAL/BIOLOGICAL PROPERTIES OF TRACER

Density, viscosity	May affect flow (e.g., high concentrations of Cl^-)
Solubility in water	Affects mobility
Sorptive properties	Affects mobility
Stability in water	Affects mobility

Physical	Chemical	Biological
radioactive decay	decomposition and precipitation	degradation

PUBLIC HEALTH CONSIDERATIONS

Toxicity
  Dilution expected
  Maximum permissible level -- determined by federal, state, provincial, and county agencies.

Proximity to drinking water

Summary of Most Important Tracers

Tracer	Characteristics
A. Particulates	
Spores	Used in karst tracing; inexpensive Detection: high, multiple tests possible by dying spores different colors Low background Moderately difficult sampling and analysis (trapping on plankton, then microscopic identification and counting) No chemical sorption May float on water, travels faster than mean flow rate
Bacteria	Most useful for studying transport of microorganisms Detection: highly sensitive Sampling: filtration, then incubation and colony counting No diffusion, slight sorption
Viruses	Detection: highly sensitive Sampling: culturing, colony counting Some sorption Smallest particulate
B. Ions (Non-radioactive, excludes dyes)	
Chloride	Conservative Inexpensive Stable Detection: 1 ppm by titration, electrical conductivity, or selective ion electrode High background may be problematic In large quantities, affects density which distorts flow No sorption
Bromide	Inexpensive Stable Detection: 0.5 ppm by selective ion electrode Low background No sorption

Tracer	Characteristics
C. Dyes	
Rhodamine WT	Used in karst and highly permeable sands and gravels Inexpensive Moderate stability Detection: 0.1 ppb by fluorimetry Low background fluorescence Moderate sorption
Fluorescein	Properties similar to Rhodamine WT, except: Degraded by sun "Chlorella" bacteria interferes High sorption
D. Radioactive Tracers	
Tritium	High stability. Detection: > 1 ppt by weak β radiation Varying background Complex analysis (expensive field and lab equipment) Half-life = 12.3 years Radiation hazard Handling and administrative problems No sorption
^{131}I	High stability Detection: high sensitivity by measuring β and α emission Background negligible Complex analysis Half-life = 8.2 days Radiation hazard Sorption on organic material
EDTA-^{51}Cr	Moderately stable (affected by cations) Detection: highly sensitive, by radiation or post-sampling neutron activation analysis No background Half-life = 28 days Radiation hazard Little sorption

Tracer	Characteristics
^{82}Br	High stability Detection: high sensitivity by measuring β emission No background Half-life = 35 hours Radiation hazard No sorption
E. Other Tracers	
Fluorocarbons	Expensive High stability Detection: 1 ppt by gas chromatography with electron capture detection Low background Difficult to maintain integrity of samples Non-degradable, volatile, low solubility, strong sorption by organic materials Low toxicity
Organic anions	Detection: few ppb by HPLC Low background Expensive analysis Very low sorption Low toxicity

APPENDIX D

CHEMICAL SUPPLY COMPANIES

A list of general chemical suppliers is provided, followed by a more specific list according to type of tracer. It is recommended that several companies be contacted, as prices can be quite variable. Prices are not quoted here because they are subject to change. Current prices can be obtained from the supplier by requesting a catalogue and price list, or by telephone inquiry.

General Chemical Supplies

Company	Telephone
J.T. Baker Chemical Company* 222 Red School Lane Phillipsburg, New Jersey 08865	(201) 859-2121
Eastman Kodak Company* 343 State Street Rochester, New York 14650	(716) 722-2915
Fisher Scientific Company* 711 Forbes Avenue Pittsburgh, Pennsylvania 15219	(412) 562-8300
Hach Company* P.O. Box 389 Loveland, Colorado 80537	(303) 669-3050
LaMotte Chemical Products Company* P.O. Box 329 Chestertown, Missouri 21620	(301) 778-3100
Union Carbide Corporation* 270 Park Avenue New York, New York 10017	(212) 551-3763

Bacteriophage

American Type Culture Collection**
12301 Parklawn Drive
Rockville, Maryland 20852

Dyes and Biological Stains

Eastman Kodak Company 343 State Street Rochester, New York 14650	(716) 722-2915
Hach Company P.O. Box 389 Loveland, Colorado 80537	(303) 669-3050
E.I. du Pont de Nemours and Company, Inc.* 1007 Market Street Wilmington, Delaware 19898	(302) 774-2421

Sources: * Analytical Chemistry Lab Guide, 1982
** Water Tracer's Cookbook (Aley, 1976)
*** Personal Communication (Thompson and Bentley, 1983)

Fluorescent Dyes

Company	Telephone
Aldrich Chemical Company, Inc.* 940 W. St. Paul Avenue Milwaukee, Wisconsin 53233	(414) 273-3850
Pylam Products Company, Inc.** 95-10 218th Street Queens Village, New York 11429	
E.I. du Pont de Nemours and Company, Inc. 1007 Market Street Wilmington, Delaware 19898	(302) 774-2421

Gases

Allied Chemical Corporation* Specialty Chemicals Division P.O. Box 2064 R Morristown, New Jersey 07960	(201) 455-4400
Union Carbide Corporation 270 Park Avenue New York, New York 10017	(212) 551-3763
AIRCO Industrial Gases* 575 Mountain Avenue Murray Hill, New Jersey 07974	(201) 464-8100
Matheson P.O. Box 85 932 Paterson Plank Road East Rutherford, New Jersey 07073	(201) 933-2400

Halogens

Alfa Products* Thiokol/Ventron Division 152 Andover Street Danvers, Mississippi 01923	(617) 777-1970
Edmund Scientific Company* 7082 Edscorp Building Barrington, New Jersey 08007	(609) 547-3488

Isotopes (Stable and Radioactive)

Company	Telephone
Monsanto Company 800 N. Lindbergh Boulevard St. Louis, Missouri 63166	(314) 694-1000
Alfa Products Thiokol/Ventron Division 152 Andover Street Danvers, Mississippi 01923	(617) 777-1970
Edmund Scientific Company 7082 Edscorp Building Barrington, New Jersey 08007	(609) 547-3488

Lycopodium Spores

Carolina Biological Supply Company**
Burlington, North Carolina 27215

Lithium

Foote Mineral Company*** Rt. 100 Exton, Pennsylvania 19341	(215) 363-6500
Lithium Corporation***	(213) 728-6658

Fluorinated Benzoic Acids

Saber Laboratory, Inc.*** Box 232 Morton Grove, Illinois 80039	(312) 998-5950
Aldrich Chemical Company, Inc. 940 W. St. Paul Avenue Milwaukee, Wisconsin 53233	(414) 273-3850

APPENDIX E

ANALYTICAL METHODS FOR THE DETECTION OF TRACERS

Electrical Conductance

An indication of the total dissolved ionic constituents can be obtained by determining the capability of the water to conduct an applied electrical current. The relative change in the ability of the ground water to conduct an electrical current (above the background resistivity prior to injection during an ion tracer test) will allow the determination of breakthrough time (travel time) of the tracer in the flow field. The ability of a solution to conduct an electrical current is a function of the concentration and charge of the ions in solution and of the rate at which the ions can move under the influence of an electrical potential. Conductivity or velocity of the ions is also a function of temperature; thus, it is important to adjust the conductivity readings for any change in temperature.

The device most commonly used for measuring electrical conductivity is a conductivity meter, read in micromhos. An alternating current is established between two points in the flow field and the conductivity (inverse of resistivity) is measured. A plot of the time versus resistivity or conductivity readings will indicate the breakthrough time of the tracer. This technique is very inexpensive and simple to use with various ionic species. The concentration of the tracer passing through a system at the breakthrough point cannot be determined by this method. It will, however, provide a quick method to determine when to sample so that concentration of tracer at the inflection point (peak conductivity) can be determined analytically.

Specific Ion Electrode

Specific ion electrode analysis is similar to pH measurement with a pH meter. Like the pH meter which measures the H^+ ion, this technique is ion-specific and thus, given data from an ionic tracer test, the concentration of the tracer can be determined using a calibration curve (millivolts versus mg/l). The reading is a function of temperature, type of ions present, and concentration of various ions particularly the ion being measured. Specific ion electrodes can be used in the field or samples can be taken and analyzed by this method in the laboratory.

Many pH meters used in the field can also read millivolts from specific ion electrodes. The electrode should be checked using a standard before initial use and should be checked daily during regular use. This method is a fast and inexpensive technique for ionic tracers which has a lower limit of detection of about 0.05 mg/liter for many constituents. Commonly, ions different than those being measured will produce part of the measured voltage, so the electrodes should be used with standard solutions having a composition similar to the water sample being measured.

Titration

Titration is the procedure by which a solution of known concentration (standard solution) is added to a water sample of unknown tracer concentration until the chemical reaction between the two solutes is complete. The point at which stoichiometrically equivalent quantities of substance have been brought together is known as the equivalence point of the titration, which is usually indicated by a change in color produced by an added dye. In acid-base titrations, organic dyes known as acid-base indicators are used for this purpose. A pH meter can be used instead of a colormetric pH indicator if greater precision is needed. The titration method of analysis varies in complexity based on the type of chemical tracer involved, and is very time-consuming if a large number of samples require analysis. Examples of tracers which can be analyzed by titrimetric techniques include Cl^-, I^-, SCN^-, NO_3^-, and SO_4^-.

Laboratory Culturing

The analysis of various bacteria, bacteriophage, and yeast as groundwater tracers requires sample collection in sterile containers (in order to minimize the potential of sample contamination by normal soil and water microorganisms) and the preparation of specific media on which to assay or culture the desired species. These microbial tracers are usually selected because of their ease of identification by a microscope on prepared media, or because they are "marked" by such characteristics as antibiotic resistance.

Once samples are collected, known volumes obtained from serial dilutions of the samples are filtered through membrane filters. These filters are then placed on prepared nutrient media plates (i.e., agar-agar or mold broth for yeast) and maintained at the optimum growth temperatures either in an incubator or at room temperature for the appropriate species-specific time period. The plates are then analyzed under a microscope for the characteristic markers such as pigmented colonies or other traits. In the case of bacteriophage, samples can be frozen at the study site and analyzed at a later date.

Microscopic Inspection of Spores

Various species of spores (i.e., Lycopodium) used as ground-water tracers are injected into the flow system at locations such as sink holes and are trapped with plankton nets at potential resurgencies. The spores (typically marked by dyes) are then examined and counted under a microscope.

Colorimetric Techniques

Analysis by colorimetric methods consists of comparing the extent of absorption of radiant energy at a particular wavelength by a solution of the test material with a series of standard solutions. Work with visual comparators requires simple equipment, but is subject to the vagaries of the human eye; in particular, fatigue and unavoidable low sensitivity under 450 nm and above 675 nm. The precision of measurement by unaided visual observation is always less than that attainable with photoelectric instruments. Such instruments, including filter photometers, are suitable for many routine methods that do not involve complex spectra. Precise work is done with a spectrophotometer which is able to employ narrow band-widths of radiant energy and which can handle absorption spectra in the ultraviolet region if equipped with fused silica optics.

The limitations of many colorimetric procedures lie in the chemical reactions upon which these procedures are based. Although very few reactions are specific for a particular substance, many reactions are quite selective, or can be rendered selective through the introduction of masking agents, control by pH, use of solvent extraction techniques, adjustment of oxidation state, or by prior removal of interferents (Dean, 1969). Both the color-developing reagent and the absorbing product must be stable for a reasonable period of time.

Numerous ground-water tracers can be analyzed by colorimetric techniques, specifically, the large class of organic dyes (see Chapter 4).

Fluorometry

Fluorometric analysis is a photoluminescent method in which the electronic state of a molecule is elevated by absorption of electromagnetic radiation, and as a consequence, the molecule emits light in order to reduce its energy and return to the ground electronic state. With the exception of X-ray fluorescence, most of the work lies in the wavelength region between 2000 and 8000 angstroms. Fluorescence provides two kinds of spectra for identification, the excitation and emission spectra.

Instruments used for fluorometric analysis range from simple filter fluorometers to highly sophisticated spectrophotofluorometers. Each will contain four principal components: (1) a source of excitation energy; (2) a sample cuvette; (3) a detector to measure the photoluminescence; and (4) a pair of filters or monochromators for selecting the excitation and emission wavelengths (Willard, 1965).

Fluorescence measurements usually are made by reference to some arbitrary chosen standard. The standard is placed in the instrument and the circuit balanced with the reading scale at any chosen setting. Without readjusting any circuit components, the standard is replaced by standard solutions of the test material and the fluorescence of each recorded. Finally, the fluorescence of the solvent and cuvette alone is measured to establish the true zero concentration.

Measurement of fluorescent intensity permits the quantitative determination of inorganic and organic species in trace amounts. Such ground-water tracers as dyes can be analyzed by this method. The technique is also very sensitive; the lower limits for the method frequently are less than those for the absorption method by a factor of ten or better, and are in the range of a few thousandths to one-tenth of a part per million.

Coulometric Techniques

Coulometric methods of analysis measure the quantity of electricity (in coulombs) required to carry out a chemical reaction. The coulomb is that amount of electricity which flows during the passage of a constant current of one ampere for one second. Reactions may be carried out either directly by oxidation or by reduction at the proper electrode (primary coulometric analysis), or indirectly by quantitative reaction in the solution with a primary reactant produced at one of the electrodes (secondary coulometric analysis). In either case, the fundamental requirement of coulometric analysis is that only one overall reaction must occur, and that the electrode reaction used for the determination proceeds with 100% current efficiency.

There are two general techniques used in coulometry. One method, the controlled-potential method, maintains a constant electrode potential by continuously monitoring the potential of the working electrode as compared to a reference electrode. The current is adjusted continuously to maintain the desired potential. The second method, known as constant-current coulometry, maintains a constant current throughout the reaction period. In this method, an excess of a redox buffer substance must be added so that the potential does not rise to a value which will cause some unwanted reaction to occur. The product of the electrolysis of the redox buffer serves as an intermediate in the reaction, and must react quantitatively with the substance to be determined.

Coulometric techniques are particularly useful in trace analyses, being accurate in the range from milligram down to microgram quantities. This technique can be used for various ionic tracers such as Cl^-, Br^-, I^-, or SCN^-.

Liquid Chromatography

Chromatography encompasses a diverse group of separation methods used to separate, isolate, and identify components of mixtures which might otherwise be resolved with great difficulty. In its broadest sense, chromatography refers to processes that are based on differences in rates at which individual components of a mixture migrate through a stationary medium under the influence of a moving phase. This rate of movement of a specific component is referred to as its retention time. Liquid chromatography is a specific class of chromatography where the mobile phase (injected sample) is a liquid and, depending on the specific method, the stationary phase is either liquid or solid.

In order to employ chromatographic techniques, the components to be separated must be soluble in the mobile phase. They must also be capable of interacting with the stationary phase either by dissolving in it, by being absorbed by it, or by reacting with it chemically. Thus, during the separations, the components become distributed between the two phases.

The most widely used chromatographic method is elution analysis. In the elution method, a small portion of sample is injected and introduced at the head of the separation column. A differential migration process occurs in which each component of the sample interacts with the stationary phase, retarding its flow at a rate characteristic of that specific component down the length of the column. The time required for a specific component to reach the end of the column, which is referred to as the retention time, is a function of the distribution coefficient of the component. The concentration of each component present is then determined based on the comparison of its retention time to that of a known concentration standard.

There are numerous chromatographic methods employing a liquid mobile phase. These include partition, adsorption, ion exchange, paper, and thin-layer chromatography. All are based on the same chromatographic principles of separation and isolation as described previously, with variation in the constituents of the mobile and stationary phases.

Liquid chromatography can be used for the analysis of a wide range of tracers at very low detection levels. Fluorinated organic acids can be detected down to concentrations from 1 ppm to 0.01 ppb using reverse phase and ion exchange high-pressure liquid chromatography (Stetzenbach, 1982). Halide tracers including Cl^-, Br^-, and I^- can be analyzed using liquid (ion exchange) chromatography.

Gas Chromatography

In gas chromatography, the components of a vaporized sample are fractionated as a consequence of partition between a mobile gaseous phase and a stationary phase which is either a liquid held on a solid support (gas-liquid chromatography) or a solid (gas-solid chromatography). In principle, gas and liquid chromatography techniques differ only in that the mobile phase in the former is a carrier gas rather than a liquid.

In gas chromatography, the sample containing the solutes is injected into a heating block where it is immediately vaporized and swept as a plug of vapor by the carrier gas stream into the column inlet. The solute components having a finite solubility in the stationary phase distribute themselves between that phase and the gas according to the equilibrium law. This partitioning process occurs repeatedly as the sample is moved toward the outlet by the carrier gas. Each component (solute) will travel at its own rate through the column, and consequently, a band corresponding to each solute will form. The bands will separate to a degree which is determined by the partition ratios of the solutes and the extent of band spreading. The solutes are eluted, one after another, in the increasing order of their partition ratios and enter a detector attached to the column exit. If a recorder is used, the signals appear on the chart as a plot of time versus the composition of the carrier gas stream. The retention time or time of emergence of a peak identifies the component, and the peak area reveals the concentration of the component in the sample. Although the gas chromatographic method is limited to volatile materials (about 15% of all organic compounds), the availability of gas chromatographs working at temperatures up to 450°C, pyrolytic techniques, and the possibility of converting many materials into a volatile derivative extend the applicability of the methods (Willard, 1965).

Gaseous tracers such as fluorocarbons (i.e., CCl_3F and CCl_2F_2) are easily detectable in low concentration of between 1 and 100 parts per trillion by gas chromatographic methods.

Mass Spectrometry

Mass spectrometry techniques involve converting the compounds of a sample into charged ionic particles consisting of the parent ion and ionic fragments of the original molecule, and resolving them according to their mass/charge ratio. A mass spectrometer consists generally of four units: (1) the inlet system; (2) the ion source; (3) the electrostatic accelerating system; and (4) the detector and readout system. This ionization process results in a mass spectrum which is a record of the numbers of different kinds of ions. The relative numbers of each type of ion are characteristic for every compound, including isomers.

Sample size requirements for solids and liquids range from a few milligrams to submicrogram quantities as long as the material can exist in the gaseous state at the temperature and pressure existing in the ion source. The average sample size for routine gas analysis is about 0.1 ml at standard conditions, but with special instrumentation, samples of 10^{-8} ml can be analyzed (Skoog, 1980). Information useful for elucidating chemical structures and for accurate determination of molecular weight can be obtained from the mass spectra literature. Mass spectra can also be employed for the quantitative analysis of complex mixtures. In such cases, the magnitude of ion currents at various mass settings is related to concentration.

Mass spectrometry is often used in conjunction with gas chromatography techniques. Such is the case for the analysis of fluorinated organic acids used as ground-water tracers. Lithium salts used for tracing are often analyzed by mass spectrometry. Stable isotopes (deuterium, tritium, ^{14}C, sulfur, etc.) are also analyzed using mass spectrometry.

Gamma-Ray Emission

Gamma emission is one type of radiation encountered in radiochemical analysis of both natural and artificial radioactive isotopes which have been used as tracers in hydrologic systems. There are three general types of radiochemical methods: (1) activation analysis; (2) isotope dilution; and (3) radiometric analysis. In activation analysis, activity is induced in one or more elements of the sample by irradiation with suitable particles and the resulting radioactivity is measured. In isotope dilution, a pure but radioactive form of the substance to be determined is mixed with the sample in a known amount. After equilibrium, a fraction of the component is isolated and its activity analyzed. In a radiometric analysis, a radioactive reagent is employed to separate completely the component from the bulk of the sample. The activity of the isolated portion is then measured.

Gamma rays (high-energy photons) are monoenergetic and have a penetrating power which is much greater than that of either alpha or beta particles, but a lower ionizing power. The gamma-ray emission spectrum, in contrast to the alpha and beta emission spectra, is characteristic for each nucleus and is thus useful for identifying radioisotopes (Skoog, 1980).

One type of detection method for gamma-ray emission is photon counting. This is a signal processing method where the individual pulse of electricity produced as a quantum of radiation is absorbed by the transducer and counted. The power of the beam is then recorded digitally in terms of counts per unit of time. This operation requires rapid response times for the detector and signal processor with respect to the rate at which quanta are absorbed by the transducer. Thus, photon counting is only applicable to beams of relatively low intensity.

Other types of detectors include gas-filled detectors, the geiger tube, proportional counters, ionization chambers, and semiconductor detectors. In most techniques, interference from alpha and beta radiation is readily avoided by filtering the beam with a thin window of aluminum or mylar. Radioactive ground-water tracers such as ^{131}I can be analyzed by gamma-ray emission.

Beta Particle Emission

Beta particle emission is another type of radiochemical analysis. Beta particles interact primarily with the electrons in the material penetrated by the particle. The molecules may be dissociated, excited, or ionized. Beta particles are produced within a nucleus by the spontaneous transformation of a neutron to a proton or a proton to a neutron.

Beta particle decay is characterized by production of particles with a continuous spectrum of energies which is characteristic of each decay process. Beta-energy ranges in air are difficult to evaluate. Thus, they are based upon the thickness of an absorber, such as aluminum, required to stop the particle. Thin-windowed geiger or proportional tube counters are used to count a uniform layer of the sample for beta sources having energies greater than 0.2 MeV. For low-energy beta emitters, such as carbon-14, sulfur-35, and tritium, a liquid scintillation counter is used. For the liquid scintillation counter method, the sample is dissolved in a solution of the scintillation compound. A vial containing the solution is then placed between two photomultiplier tubes housed in a light-tight container. The output from the two tubes is fed into a counter which records a count only when pulses from the two detectors arrive at the same time.

Beta particle emission techniques are used for analysis of radioactive tracers.

Neutron Activation Analysis

Neutron activation analysis involves the production of a radioactive isotope by the capture of neutrons by the nuclei of the substance to be analyzed. Irradiation is accomplished by placing the sample to be analyzed in an intense flux of either thermal or fast neutrons for a length of time sufficient to produce a measurable amount of the desired radioisotope. Radiation detectors are used to analyze the radiation emitted by each sample and the unique radiation characteristics of the sample are sought.

The method known as post-sampling activation analysis has been described by Schmotzer (1973) as a tracer technique using low concentrations of Br^-. Although this method of tracer analysis reduces the amount and subsequently the cost of the chemical tracer, it is a very expensive technique.

REFERENCES

Akamatsu, K., and Matsuo, M., 1973, Safety of optical whitening agents (in Japanese): Senryo to Yakuhin, Vol. 18, No. 2, pp. 2-11.

Alburger, J. R., 1977, Leak testing with dyed liquid tracers: Materials Evaluation, Dec., pp. 60-64.

Aley, T., and Fletcher, M. W., 1976, Water tracer's cookbook: Journal of the Missouri Speleological Survey, Vol. 16, No. 3.

Allen, M. J., and Morrison, S. M., 1973, Bacterial movement through fractured bedrock: Ground Water, Vol. 11, No. 2, pp. 6-10.

Andre, J. C., and Molinari, J., 1976, Mises au point sur les differents facteurs physiochimique influant sur la mesure de concentration de traceurs fluorescents et leurs consequences practiques en hydrologie: Journal of Hydrology, Vol. 30, pp. 257-286.

Andrews, J. H., Lee, D. J., 1979, Inert gases in groundwater from the Bunter Sandstone of England as indicators of age and paleoclimatic trends: Journal of Hydrology, Vol. 41, pp. 233-252.

Arandjelovic, D., 1969, A possible way of tracing groundwater flows in karst: Geophysical Prospecting, Vol. 17, No. 4, pp. 404-418.

Arandjelovic, D., 1977, Determining groundwater flow in karst using "Geobomb." In Karst Hydrology, edited by J. S. Tolson and F. L. Doyle: Memoirs of the 12th Congress of the Int. Assoc. Hydrogeologists, University of Alabama Press in Huntsville, pp. 399-400.

Atkinson, T. C., 1968, Tracing swallet waters using locopodium spores: Transactions Cave Research Group of Great Britain, Vol. 10, No. 2, pp. 99-106.

Atkinson, T. C., Drew, D. P., and High, C., 1967, Mendip karst hydrology research project, phases one and two. Occasional Publ. Wessex Cave Club, Vol. 2, No. 1, 38 p.

Atkinson, T. C., Smith, D. I., Lavis, J. J., and Whitaker, R. J., 1973, Experiments in tracing underground waters in limestones. Journal of Hydrology, Vol. 19, pp. 323-349.

Aulenbach, D. B., Bull, J. H., and Middlesworth, B. C., 1978, Use of tracers to confirm ground-water flow: Ground Water, Vol. 16, No. 3, pp. 149-157.

Aulenbach, D. B., and Clesceri, N. L., 1980, Monitoring for land application of wastewater: Water, Air, and Soil Pollution, Vol. 14, pp. 81-94.

Bear, J., 1961, On the tensor form of dispersion in porous media, J. Geophys. Res., 66(4), pp. 1185-1197.

Bear, J., 1969, Hydrodynamic dispersion, in Flow Through Porous Media, DeWiest (Ed.), Academic Press.

Bentley, H. W., and Alweis, S., 1982, Use of sulfur isotopes to evaluate groundwater contamination by mining and industrial processes, ACS Symposium on the Hydrology of Mining and Industrial Wastes, El Paso, December 2 (abstracts with programs).

Borg, I. Y., and others, 1976, Information pertinent to the migration of radionuclides in ground water at the Nevada Test Site: Lawrence Livermore Laboratory, University of California, Publication UCRL-52078 Part I, 216 p.

Bouwer, H., 1978, Groundwater Hydrology: New York, McGraw-Hill Book Co., 480 p.

Brown, E., Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U. S. Geological Survey Tech. Water Resources Investigation, Vol. 5, No. A1, 160 p.

Brown, J. D., 1980, Evaluation of fluorocarbon compounds as ground-water tracers: Soil column studies: Unpublished M.S. thesis, University of Arizona, Department of Hydrology and Water Resources, 97 p.

Brown, M. C., and Ford, D. C., 1971, Quantitative tracer methods for investigation of karst hydrology systems, with reference to the Maligne Basin area: Transactions of the Cave Research Group of Great Britain, Vol. 13, No. 1, pp. 37-51.

Brown, M. C., Wigley, T. L., and Ford, D. C., 1969, Water budget studies in karst aquifers: Journal of Hydrology, 9(1), pp. 113-116.

Buchtela, K., Mairhofer, J., Maurin, V., Papadimitropoulos, T., and Zotl, J., 1968, Comparative investigations into recent methods of tracing subterranean water. National Speleological Society Bulletin, Vol. 30, 13, pp. 179-195.

Burdon, D. J., et al., 1963, The use of tritium in tracing karst ground water in Greece, in Radioisotopes in Hydrology IAEA Symposium, Tokyo, pp. 309-320.

Buss, D. F., and Bandt, K. E., 1981, An all-teflon bailer and an air-driven pump for evacuating small-diameter ground-water wells: Ground Water, Vol. 19, No. 4, pp. 100-102.

California Department of Water Resources, 1968, Water well standards, State of California: Calif. Dept. Water Res. Bulletin, Vol. 74, 205 p.

Campbell, M. D., and Lehr, J. H., 1973, Water well technology: McGraw-Hill, New York, 681 p.

Carrera, J., and Walter, G. R., 1985 CONFLO, a new numerical model for analyzing convergent flow tracer tests. Sandia Contractors Report (in preparation).

Carter, R. C., and others, 1959, Helium as a ground-water tracer. Journal of Geophysical Research, Vol. 64, pp. 2433-2439.

Cherry, J. A., and Johnson, P. E., 1982, A multilevel device for monitoring in fractured rock: Ground Water Monitoring Review, Summer 1982, pp. 41-44.

Claassen, H. C., and Cordes, E. H., 1975, Two-well recirculating tracer test in fractured carbonate rock, Nevada: Hydrological Sciences Bulletin 20(3), pp. 367-382.

Coleman, D. D., Meents, W. F., Liu, C. L., and Keogh, R. A., 1977, Isotopic identification of leakage gas from underground storage reservoirs -- a progress report: Illinois State Geological Survey, Illinois Petroleum No. 111, 10 p.

Combarnous, M. A., and Bories, S. A., 1975, Hydrothermal convection in saturated porous media, *in* Advances in Hydroscience, V. T. Chow (ed.): pp. 232-307.

Corey, J. C., 1968, Evaluation of dyes for tracing water movement in acid soils: Soil Science, Vol. 106, No. 3, pp. 182-187.

Cory, C. C., and Horton, J. H., 1968, Movement of water tagged with ^{2}H, ^{3}H, and ^{18}O through acidic kaolinitic soil: Soil Sci. Soc. America Proc., Vol. 32, pp. 471-475.

Cotlove, E., 1964, Determination of chloride in biological materials: Meth. Biochem. Anal., Vol. 12, 287 p.

Custodio, E., 1976, Trazadores y tecnicas radioisotopicas en hidrologia subterranea, Section 12 in Hidrologia Suberrranea, Vol. 2, edited by E. Custodio and M. R. Llamas; Ediciones Omega, Barcelona, Spain, pp. 1165-1312.

Dansgaard, W., 1964, Stable isotopes in precipitations: Tellus, Vol. 16, pp. 436-468.

Davis, J. T., Flotz, E., and Balkemore, W. S., 1970, *Serratia marcescens*, a pathogen of increasing clinical importance: J. Am. Med. Assoc., Vol. 214, pp. 145-150.

Davis, S. N., 1969, Porosity and permeability of natural materials, *in* Flow through porous media, R. M. DeWiest, ed., Academic Press, New York, pp. 54-89.

Davis, S. N., and Bentley, H. W., 1982, Dating groundwater, a short review, in Nuclear and chemical dating techniques, Lloyd Curie, ed., Am. Chemical Society Symposium Series No. 176, Chapter 11, pp. 187-222.

Davis, S. N., and DeWiest, R. J. M., 1966, Hydrogeology: John Wiley and Sons, New York, 463 p.

Davis, S. N., Thompson, G. M., Bentley, H. W., and Stiles, G., 1980, Groundwater tracers -- a short review: Ground Water, Vol. 18, pp. 14-23.

Dean, J. A., 1968, Chemical Separation Methods: D. Van Nostrand, New York.

Dole, R. B., 1906, Use of fluorescein in the study of underground water: U. S. Geological Survey Water Supply and Irrigation Paper, No. 160, pp. 73-83.

Downs, W. F., McAtee, R. E., and Capuano, R. M., 1983, Tracer injection tests in a fracture dominated geothermal system (Abstract): Am. Geophysical Union, EOS, Vol. 64, No. 18, p. 229.

Drew, D. P., 1968, A study of the limestone hydrology of St. Dunstans Well and Ashwick drainage basins, Eastern Mendip: Proc. Univ. Bristol Speleol. Soc., Vol. 11, No. 3, pp. 257-276.

Drew, D. P., and Smith, D. I., 1969, Techniques for the tracing of subterranean drainage: Br. Geomorphol. Res. Group Tech. Bulletin, Vol. 2, 36 p.

Drewry, W. A., and Eliassen, R., 1967, Virus movement in ground water: Jour. Water Pollution Control Federation, Vol. 40, No. 4, pp. 257-271.

Drost, W., Klotz, D., Koch, A., Moser, H., Neumaier, F., and Ravert, W., 1968, Point dilution methods of investigating ground-water flow by means of radioisotopes: Water Resources Research, Vol. 4, pp. 125-146.

Dunn, J. A., 1963a, New method of water tracing: Journal of Eldon Pothole Club, Vol. 5, p. 5.

Ellis, J., 1980, A convenient parameter for tracing leachate from sanitary landfills: Water Research 14(9): pp. 1283-1287.

Elrick, D. E., and Lawson, D. W., 1969, Tracer techniques in hydrology, Proceedings of the Canadian Hydrology Symposium No. 7: National Research Council of Canada, Subcommittee on Hydrology, (1), pp. 155-187.

Ferronsky, V. I., and Polyakov, V. A., 1982, Environmental isotopes in the hydrosphere: John Wiley and Sons, Interscience Publications, New York, 466 p.

Fetter, C. W., Jr., 1980, Applied hydrogeology: Columbus, Ohio, Charles E. Merrill Publishing Co., 488 p.

Fetter, C. W., Jr., 1981, Determination of the direction of ground water flow: Ground Water Monitoring Review: Vol. 1, No. 3, pp. 28-31.

Feuerstein, D. L., and Selleck, R. E., 1963, Fluorescent tracers for dispersion measurements: Journal of the American Society of Civil Engineers, August, pp. 1-21.

Fletcher, M. W., and Myers, R. L., 1974, Ground-water tracing in karst terrain using phage T-4: Amer. Soc. Microbiol. Abstr. Ann. Mtg., p. 52.

Fontes, J. C., and Fritz, P., 1975, Isotope hydrology 1974 -- a review of the IAEA Symposium on isotope techniques in groundwater hydrology: Earth and Planetary Science Letters, Vol. 4, pp. 321-324.

Fontes, J. C., and Garnier, J. M., 1979, Determination of the initial ^{14}C activity of the total dissolved carbon, A review of the existing models and a new approach: Water Resources Research, Vol. 15, No. 2, pp. 399-413.

Fox, C. S., 1952, Radioactive isotopes trace underground waters: Public Works, Vol. 83, pp. 57-58.

Freeze, R. A., and Cherry, J. A., 1979, Groundwater: Prentice-Hall, Inc., New Jersey, 604 p.

Fried, J. J., 1975, Groundwater pollution; theory, methodology modeling, and practical rules. Elsevier Scientific Publishing Co., pp. 59-113.

Gann, E. E., and Harvey, E. J., 1975, Norman Creek: A source of recharge to Maramec Spring, Phelps County, Missouri: Journal of Research of the U. S. Geological Survey, Vol. 3, No. 1, pp. 99-102.

Gardner, G. D., and Gray, R. E., 1976, Tracing subsurface flow in karst regions using artificially colored spores: Association of Engineering Geologists Bulletin, Vol. 13, pp. 177-197.

Gaspar, E., and Oncescu, M., 1972, Radioactive tracers in hydrology: Elsevier Publishing Co., pp. 77-154.

Gat, J. R., 1971, Comments on the stable isotope method in regional groundwater investigations: Water Resources Research, Vol. 7, pp. 980-993.

Gelhar, L. W., 1982, Analysis of two-well tracer tests with a pulse input: Rockwell International (Hanford, Washington) Report RHO-BW-CR-131P, 96 p.

Gelhar, L. W., and Collins, M. A., 1971, General analysis of longitudinal dispersion in nonuniform flow: Water Resource Research 7(6), pp. 1511-1521.

Gelhar, L. W., Gutjahr, A. L., and Naff, R. L., Stochastic analysis of macrodispersion in a stratified aquifer, Water Resources Research, Vol. 15(6), pp. 1387-1397.

Gillham, R. W., and Johnson, P. E., 1981, A positive displacement groundwater sampling device: Ground Water Monitoring Review, Summer 1981, pp. 33-35.

Glover, R. R., 1972, Optical brighteners -- a new water tracing reagent. Transactions Cave Research Group, Great Britain, Vol. 14, No. 2, pp. 84-88.

Goyal, S. M., Zerda, K. Z., and Gerba, C. P., 1980, Concentration of coliphages from large volumes of water and waste water: Appl. Environ. Microbiol., Vol. 39, pp. 85-91.

Greenkorn, Robert A., 1962, Experimental study of waterflood tracers: Journal of Petroleum Technology, January, pp. 87-92.

Grisak, G. E., and Pickens, J. F., 1980, Solute transport through fractured media 1. The effect of matrix diffusion: Water Resources Research, Vol. 16, No. 4, pp. 719-730.

Grisak, G. E., Pickens, J. F., and Cherry, J. A., 1979, Solute transport through fractured media 2. Column study of fractured till: manuscript submitted to Water Resources Research, July, 1979.

Grove, D. B., and Beetem, W. A., 1971, Porosity and dispersion constant calculations for a fractured carbonate aquifer using the two-well tracer method: Water Resources Research, Vol. 7, No. 1, pp. 128-134.

Haas, J. L., 1959, Evaluation of groundwater tracing methods used in speleology: Bulletin Natl. Spel. Soc. (U. S. A.), 21(2), pp. 67-76.

Hach Chemical Company, 1969, Colorimetric procedures and chemicals for water and wastewater analysis: Hach Chem. Co., Ames, Iowa, 91 p.

Hagedorn, C., Hansen, D. T., and Simonson, G. H., 1978, Survival and movement of fecal indicator bacteria in soil under conditions of saturated flow: J. Environ. Quality, Vol. 17, pp. 55-59.

Halevy, E., and Nir, A., 1962, The determination of aquifer parameters with the aid of radioactive tracers: Jour. Geophysical Research, Vol. 61, pp. 2403-2409.

Heath and Trainer, 1968, Introduction to Ground-Water Hydrology: John Wiley and Sons, New York, 283 p.

Higgins, C. H., 1969, Evaluation of the ground-water contamination hazard from underground nuclear explosions: Jour. Geophys. Research, Vol. 64, p. 1509.

Hubbard, E. F., Kilpatrick, F. A., Martens, L. A., and Wilson, J. F., Jr., 1982, Measurement of time of travel and dispersion in streams by dye tracing, in: Techniques of Water Resources Investigations of the U. S. G. S., Chapter A9, Book 3, Applications of Hydraulics.

HydroGeoChem, 1984, Hydrologic investigation of existing pond seepage at Jim Budger power plant, Report to Pacific Power and Light, Portland, Oregon.

Isotope Hydrology Section, International Atomic Energy Agency, 1973, Nuclear techniques in ground-water hydrology, In: Ground-water studies: UNESCO, Paris, Sections 10.1-10.4, 38 p.

Ivanovich, M., and Smith, D. B., 1978, Determination of aquifer parameters by a two-well pulse method using radioactive tracers, Journal of Hydrology, Vol. 36, No. 1/2, pp. 35-45.

Jennings, A. R., and Schroeder, M. C., 1968, Laboratory evaluation of selected radioisotopes as ground-water tracers: Water Resources Research, Vol. 4, pp. 829-838.

Johnson Division, UOP, Inc., 1972, Ground water and wells, 2nd ed.: Edward E. Johnson, Co., St. Paul, Minnesota, 440 p.

Kaas, W., 1964, Die unmittelbare Bestimmung von Uranin-Spuren bei Farbversuchen: Steirische Beitrage zur Hydrogeologie. Jahrgang 1963/64, pp. 37-66.

Kaufman, W. J., 1961, Tritium as a ground-water tracer: Am. Soc. Civil Eng. Trans. Paper 3203, pp. 436-446.

Kaufman, W. J., and Orlob, G. T., 1956, Measuring ground-water movements with radioactive and chemical tracers: Amer. Waterworks Association Journal, 48, pp. 559-572.

Keely, J. F., 1984, Optimizing pumping strategies for contaminant studies and remedial actions: Ground Water Monitoring Review, Vol. 4, No. 3, pp. 63-74.

Keith, S. J., Wilson, L. G., Fitch, H. R., Esposito, D. M., 1982, Sources of spatial-temporal variability in ground-water quality data and methods of control: Case study of the Cortaro Monitoring Program, Arizona: Second National Symposium on Aquifer Restoration and Ground-Water Monitoring, National Water Well Assoc., Worthington, Ohio, pp. 217-227.

Keswick, B. H., Wang, D., and Gerba, C. P., 1982, The use of Microorganisms as Ground-Water Tracers; A Review: Ground Water, Vol. 20, No. 2, pp. 142-149.

Keys, W. S., and Brown, R. F., 1978, The use of temperature logs to trace the movement of injected water: Ground Water, Vol. 16, No. 1, pp. 32-48.

Keys, W. S., and MacCary, L. M., 1971, Application of borehole geophysics to water-resources investigations: U. S. Geological Survey Techniques in Water Resources Inv., Book 2, Chapter 1.

Kilpatrick, F. A., Sayre, W. W., and Richardson, E. V., 1967, (Discussion of Repogle et al.), Flow measurements with fluorescent tracers (loc. cit): Proceedings of the ASCE, Journal of the Hydraulics Division, 93, pp. 298-308.

Klotz, D., Moser, H., and Trimborn, P., 1978, Single-borehole techniques; present status and examples of recent applications: Isotope Hydrology, IAEA, Vienna, Part 1, pp. 159-179.

Knuttson, G., 1968, Tracers for ground-water investigations, in: Ground Water Problems. Eriksson, E., Gustafsson, Y., and Nilsson, K., (eds): Pergamon Press, London, pp. 123-152.

Koerner, R. M., Reif, J. S., and Burlingame, M. J., 1979, Detection methods for location of subsurface water and seepage: Journal of the Geotechnical Engineering Division, ASCE, Vol. 105, pp. 1301-1316.

Konikow, L. F., and Bredehoeft, J. D., 1974, Modeling flow and chemical quality changes in an irrigated stream-aquifer system, Water Resources Research, Vol. 10(3), pp. 562-596.

Krothe, N. C., 1982, Sulfur isotopes and hydrochemical variations as an indicator of flow in groundwater: in Isotope studies of hydrologic processes, E. C. Perry, Jr. and C. W. Montgomery, editors: Northern Illinois University Press, DeKalb, Illinois, pp. 75-82.

Lange, A. L., 1972, Mapping underground streams using discrete natural noise signals: A proposed method: Caves and Karst, Vol. 14, pp. 41-44.

Lee, R., Cherry, J. A., and Pickens, J. F., 1980, Groundwater transport of a salt tracer through a sandy lakebed: Limnol. Oceanogr. 25(1), pp. 45-61.

Lenda, A., and Zuber, A., 1970, Tracer dispersion in groundwater experiments: Isotope Hydrology (Proc. Symp. Vienna, 1970), IAEA, pp. 619-641.

Lewis, D. C., Kriz, G. J., and Burgy, R. H., 1966, Tracer dilution sampling technique to determine hydraulic conductivity of fractured rock: Water Resources Research, Vol. 2, pp. 533-542.

Libby, W. F., 1961, Tritium Geophysics: Jour. Geophys. Research, Vol. 66, pp. 3767-3782.

Loosli, H. H., and Oeschger, H., 1978, Argon-39, carbon-14, and krypton-85 measurements in groundwater samples, In: Isotope Hydrology 1978: Internat. Atomic Energy Agency, Vienna, Vol. 2, pp. 931-945.

Malcolm, R. L., Aiken, G. R., Thurman, E. M., and Avery, P. A., 1980, Hydrophilic organic solutes as tracers in groundwater recharge studies: Contaminants and Sediments, Vol. 1, pp. 71-87.

Marston, T. K., and Schofield, J., 1962, An improved method of tracing underground waters using Rhodamine B: Cave Research Group Newsletter, No. 84, pp. 4-13.

Martin, R., and Thomas A., 1974, An example of the use of bacteriophage as a ground-water tracer: Journal of Hydrology, Vol. 23, pp. 73-78.

Mather, J. D., Gray, D. A., and Jenkins, D. G., 1969, The use of tracers to investigate the relationship between mining subsidence and groundwater occurrence of Aberdare, South Wales: Journal of Hydrology, Vol. 9, pp. 136-154.

Mattson, S., 1929, The laws of soil colloidal behavior I: Soil Science, Vol. 27-28, pp. 179-220.

Maurin, V., and Zotl, J., 1959, Die Untersuchung der Zusammenhange unteirir-discher Wasser nit besonderer Berucksichtigung der Karstver haltnisse: Steierische Beitrage zur Hydrologie, Jahrgang, 1959, Graz, Austria.

Mayr, A., 1953, Bluten pollen und Pflanzl Sporen als Mittel zur Untersuchung von Quellen und Karstwassen: Anz. Math-Natw. Kl. Ost. Ak. Wiss.

Mazor, E., 1972, Paleotemperatures and other hydrological parameters deduced from noble gases dissolved in ground waters, Jordan Rift Valley, Israel: Geochimica et Cosmochimica Acta: Vol. 36, pp. 1321-1336.

Mazor, E., 1976, The Ram Crater Lake, a note on the revival of a 2,000-year-old ground-water tracing experiment: in Interpretation of Environmental Isotope and Hydrochemical Data. in Groundwater Hydrology. IAEA, Vienna, pp. 179-181.

McLaughlin, M. J., 1982, A review of the use of dyes as soil water tracers: Water S. A., Water Research Commission, Pretoria, South Africa, Vol. 8, No. 4, pp. 196-201.

Morrison, R. D., and Brewer, P. E., 1981, Air-lift samplers for zone-of-saturation monitoring: Ground Water Monitoring Review, Spring 1981, pp. 52-55.

Murray, J. P., Rouse, J. V., and Carpenter, A. B., 1981, Groundwater contamination by sanitary landfill leachate and domestic wastewater in carbonate terrain: principle source diagnosis, chemical transport characteristics and design implications: Water Research, 15(6), pp. 745-757.

Naymik, T. G., and Sievers, M. E., 1983, Ground-water tracer experiment (II) at Sand Ridge State Forest, Illinois: Illinois State Water Survey Division, SWS Contract Report 334, 105 p.

Ogato, A., and Banks, R. B., 1961, A solution of the differential equation of longitudinal dispersion in porous media, U. S. Geological Survey, Professional Paper 411A.

Omoti, O., 1977, Laboratory and field studies of pathways of solute movement in soils: unpublished Ph.D. dissertation, University of Reading, England.

Ormerod, J. G., 1964, Serratia indica as a bacterial tracer for water movement: Appl. Bact., Vol. 27, pp. 342-349.

Payne, B. R., 1972, Isotope hydrology, in V. T. Chow, editor, Advances in Hydroscience, Vol. 8, pp. 95-138.

Pearson, F. J., Jr., White, D. E., Carbon-14 ages and flow rates of water in Carrizo Sand, Atascosa County, Texas: Water Resources Research, Vol. 3, No. 1, pp. 251-261.

Perkins, T. K., and Johnston, O. C., 1963, A review of diffusion and dispersion in porous media, Soc. Pet. Eng. Jour., Vol. 3(1), pp. 70-84.

Pickens, J. F., Cherry, J. A., Coupland, R. M., Grisak, G. E., Merrit, W. F., and Risto, B.A., 1981, A multilevel device for ground-water sampling: Ground Water Monitoring Review, Spring 1981, pp. 48-51.

Pickens, J. F., and Grisak, G. E., 1981, Scale-dependent dispersion in a stratified granular aquifer. Submitted to Water Resources Research, January, 1981, pp. 1-83.

Pickens, J. F., Merritt, W. F., and Cherry, J. A., 1976, Field determination of the physical contaminant transport parameters in a sandy aquifer. Paper presented at the Advisory Group Meeting on "The Use of Nuclear Techniques in Water Pollution Studies."

Pickett, E. E., and Koirtyohann, S. R., 1969, Emission flame photometry--a new look at an old method: Analyt. Chem., Vol. 45, pp. 28a-42a.

Pinder, G. F., 1973, A Galerkin-finite element simulation of ground-water contamination on Long Island, New York, Water Resources Research, Vol. 10(3), pp. 546-562.

Plata Bedmar, A., 1972, Isotopos en Hidrologia: Editorial Alhambra, S. A., Madrid, 328 p.

Pyle, B. H., and Thorpe, H. R., 1981, Evaluation of the potential for microbiological contamination of an aquifer using a bacterial tracer: Proceedings of Ground-Water Pollution Conference, 1979. Australian Water Resources Council Conference Series, No. 1, pp. 213-224.

Rahe, T. M., Hagedorn, C., McCoy, E. L., and Kling, G. F., 1978, Transport of antibiotic-resistant *Echerichia coli* through western Oregon hill slope soils under conditions of saturated flow: J. Environ. Qual., Vol. 7, pp. 487-494.

Repogle, J. A., Myers, L. E., and Brust, K. J., 1966, Flow measurements with fluorescent tracers: Journal of the Hydraulics Division ASCE, Vol. 92, pp. 1-15.

Reynolds, E. R. C., 1966, The percolation of rainwater through soil demonstrated by fluorescent dyes: Journal of Soil Science, Vol. 17, No. 1, pp. 127-132.

Reznek, S., Hayden, W., and Lee, M., 1979, Analytical note -- fluorescein tracer technique for detection of ground-water contamination: Journal of the American Water Works Association, Vol. 71, No. 10, pp. 586-587.

Rippon, J. E., 1963, The use of a colored bacterium as an indicator of local water movement: Chem. Ind., Vol. 11, pp. 445-446.

Robertson, J. B., 1969, Behavior of xenon-133 gas after injection underground: U. S. Geol. Survey Open File Report ID022051, 37 p.

Robin, M. J. L., Dytynyshyn, D. J., and Sweeney, S. J., 1982, Two gas-drive sampling devices: Ground Water Monitoring Review, Winter 1982, pp. 63-66.

Rodrigeuz, C. O., 1977, Hidrologia isotopica en Colombia: Instituto de Asuntos Nucleares, Bogota, 81 p.

Rogers, A. S., 1958, Physical behavior and geologic control of radon in mountain streams: U. S. Geological Survey Bulletin 1052E, pp. 187-211.

Romero, J. C., 1970, The movement of bacteria and viruses through porous media: Ground Water, Vol. 8, No. 2, pp. 37-48.

Rorabaugh, M. I., 1956, Ground water in northeastern Louisville, Kentucky: U. S. Geol. Survey Water-Supply Paper 1360-B, pp. 101-169.

Saleem, M., 1971, A simple method of ground water direction measurement in a single borehole: Journal of Hydrology, 12, pp. 387-410.

Sanitary Engineering Research Laboratory, University of California, Berkeley, 1954, Report on the investigation of travel of pollution: California State Water Pollution Control Board Pub. 11, 218 p.

Sargeant, K., 1969, The deep culture of bacteriophage, *in* Methods in Microbiology, Norris, J. R., and Ribbons, D. W., (eds.), Vol. 1: Academic Press, New York, pp. 505-520.

Sauty, J. P., 1978, Identification of hydrodispersive mass transfer parameters in aquifers by interpretation of tracer experiments in radial converging or diverging flow (in French): Journal of Hydrology, Vol. 39, pp. 69-103.

Sauty, J. P., 1980, An analysis of hydrodispersive transfer in aquifers: Water Resources Research, Vol. 16, No. 1, pp. 145-158.

Scandura, J. E., and Sobsey, M. D., 1981, Survival and fate of enteric viruses in on-site waste-water disposal systems in coastal plains soils: Abs. Ann. Mtg. Am. Soc. Microbiol., p. 175.

Schaub, S. A., Meier, E. P., Kolmer, J. R., and Sorber, C. A., 1975, Land application of wastewater: the fate of viruses, bacteria, and heavy metals at a rapid infiltration site: Report No. TR 7504, AD A011263, U. S. Army Medical Bioengineering Research and Development Laboratory, Ft. Detrick, Frederick, Maryland.

Schaub, S. A., and Sorber, C. A., 1977, Virus and bacteria removed from waste water by rapid infiltration through soil: Applied Environmental Microbiology, Vol. 33, pp. 609-619.

Scheidegger, A. E., 1954, Statistical hydrodynamics in porous media, J. Applied Physics, Vol. 25(8), pp. 994-1001.

Schmidt, K. D., 1977, Water quality variations for pumping wells: Ground Water, Vol. 15, No. 2, pp. 130-137.

Schmotzer, J. K., Jester, W. A., and Parizek, R. R., 1973, Groundwater tracing with post sampling activation analysis: Journal of Hydrology, Vol. 20, pp. 217-236.

Simpson, E. S., 1984, Personal communication, Department of Hydrology, University of Arizona, June, 1984.

Simpson, E. S., Neuman, S. P., and Thompson, G. M., 1983, Field and theoretical investigations of mass and energy transport in subsurface materials: Progress Report for the Nuclear Regulatory Commission by the Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona.

Sinton, L. W., 1980, Investigations into the use of the bacterial species Bacillus stearothermophilus and Echerichia coli as tracers of ground-water movement: Water and Soil Technical Publication No. 17, MWD, Wellington, 24 p.

Sklash, M. G., and Farvolden, R. N., 1979, The role of groundwater in storm runoff: Journal of Hydrology, Vol. 43, pp. 45-65.

Skoog, D. A., and West, D. M., 1980, Principles of instrumental analysis: Holt, Rinehart, and Winston, Philadelphia, Pennsylvania, 2nd edition, p. 760.

Slichter, C. S., 1902, The motions of underground waters: U. S. Geological Survey Water-Supply Paper No. 67, p. 106.

Slichter, C. S., 1905, Field measurements of the rate of movement of underground waters: U. S. Geological Survey Water Supply and Irrigation Paper No. 140, pp. 9-34.

Smart, P. L., 1976, Catchment delimitation in karst areas by the use of qualitative tracer methods: Proc. 3rd Internatl. Symp. of Underground Water Tracing, Bled, Yugoslavia, 1976, pp. 291-298.

Smart, P. L., and Laidlaw, I. M. S., 1977, An evaluation of some fluorescent dyes for water tracing: Water Resources Research, Vol. 13, No. 1, pp. 15-33.

Smart, P. L., and Smith, D. I., 1976, Water tracing in tropical regions; the use of fluorometric techniques in Jamaica: Journal of Hydrology, Vol. 30, pp. 179-195.

Smith, D. B., 1973, Flow tracing using isotopes: Groundwater Pollution in Europe, Proc. Reading Conf., Water Research Association, pp. 241-250.

Smith, S. J., and Davies, R. J., 1974, Relative movement of bromide and nitrate through soils: Jour. Environmental Quality, Vol. 3, pp. 152-155.

Sorey, M. L., 1971, Measurement of vertical ground-water velocity from temperature profiles in wells: Water Resources Research, Vol. 7, No. 4, pp. 963-970.

Stallman, R. W., 1963, Computation of ground-water velocity from temperature data: in U. S. Geological Survey Water Supply Paper 1544-H., R. Bental (ed.), pp. 36-46.

Stetzenbach, K. J., Jensen, S. L., and Thompson, G. M., 1982, Trace enrichment of fluorinated organic acids used as ground-water tracers by liquid chromatography: Environmental Science and Technology, Vol. 16, p. 250.

Sudicky, E. A., and Cherry, J. A., 1979, Field observations of tracer dispersion under natural flow conditions in an unconfined sandy aquifer, Water Pollution Research (Canada), Vol. 14.

Sugisaki, R., 1969, Measurement of effective flow velocity of groundwater by means of dissolved gases: American Jour. Science, Vol. 259, pp. 144-153.

Tennyson, L. C., and Settergren, C. D., 1980, Percolate water and bromide movement in the root zone of effluent irrigation sites: Water Resources Bulletin, Vol. 16, No. 3, pp. 433-437.

Tester, J. W., Bivens, R. L., and Potter, R. M., 1982, Interwell tracer analysis of a hydraulically fractured grantitic geothermal reservoir: Society of Petroleum Engineers Journal, August, 1982, pp. 537-554.

Theis, C. V., 1963, Hydrologic phenomena affecting the use of tracers in timing ground-water flow: Radioisotopes in Hydrology. International Atomic Energy Agency (Tokyo Symposium) Vienna, Austria, pp. 193-206.

Thompson, G. M., and Hayes, J. M., 1978, Trichlorofluoromethane in ground water. A possible tracer and indicator of ground-water age: Water Resources Research, Vol. 15, No. 3, pp. 546-554.

Thompson, G. M., Hayes, J. M., and Davis, S. N., 1974, Fluorocarbon tracers in hydrology: Geophysical Research Letters, Vol. 1, pp. 177-180.

Thompson, G. M., and Jensen, S. L., 1980, (unpublished manuscript), New organic tracers for waste monitoring: Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona.

Thorp, J., and Gamble, E. E., 1972, Annual fluctuation of water levels in the soils of the Miami catena, Wayne County, Indiana: Earlham College, Science Bulletin No. 5, 26 p.

Thorpe, H. R., 1979, Movement of contaminants into and through the Heretaunga Plains Aquifers, Hawkes Bay, New Zealand: Paper presented at AWRC Conference on Groundwater Pollution, Perth, Australia.

Todd, D. K., 1980, Groundwater hydrology, 2nd ed.: John Wiley and Sons, New York, 535 p.

U. S. Department of the Interior, 1969, Methods for chemical analysis of water and wastes: Federal Water Pollution Control Admin., Cincinnati, Ohio, 280 p.

Vecchioli, J., Ehrlich, G. G., and Ehlke, T. A., 1972, Travel of pollution indicator bacteria through the Magothy aquifer, Long Island, New York: U. S. Geological Survey Prof. Paper 800-B., pp. B237-B239.

Vogel, J. C., Thilo, L., Van Dijken, M., 1974, Determination of groundwater recharge with tritium, Journal of Hydrology, Vol. 23, pp. 131-140.

Vuataz, F. D., Stix, J., Goff, F., and Pearson, C. F., 1984, Low-temperature geothermal potential of the Ojo Caliente warm springs area in northern New Mexico: Los Alamos National Laboratory Publication LA-10105-OBES, VC-666, 56 p.

Wagner, O. R., 1977, The use of tracers in diagnosing interwell reservoir heterogeneities: Jour. Petroleum Technology, November, 1977, pp. 1410-1416.

Warren, J. E., and Skiba, F. F., 1964, Macroscopic dispersion, Soc. Pet. Eng. Jour., Vol. 4(3), pp. 215-230.

Water and Power Resources Service, 1981, Ground water manual: U. S. Department of the Interior, Denver, Colorado, 480 p.

Webster, D. S., Proctor, J. F., and Marine, I. W., 1970, Two-well tracer test in fractured crystalline rock: U. S. Geological Survey Water Supply Paper 1544-I, pp. 1-22.

White, K. E., 1981, Hydrological studies possible with radionuclides of bomb-test. Primordial and natural origin to complement investigations using manufactured radiotracers: Water Pollution Control, 80(4), pp. 498-512.

Willard, H. H., Merritt, L. L. Jr., and Dean, John A., 1965, Instrumental methods of analysis, D. Van Nostrand, New York, 5th ed., 859 p.

Wilson, J. F., 1968, Fluorometric procedures for dye tracing: Chapter A12 in Techniques of Water-Resources Investigations of the U.S.G.S., U. S. Geological Survey, pp. 1-31.

Wilson, L. G., 1971, Investigations on the subsurface disposal of waste effluent at inland sites: Water Resources Research Center, Tucson, Arizona, Final report to Office of Saline Water, Grant #14-01-0001-1805, pp. 1-82.

Wimpenny, J. W. T., Cotton, N., and Strathem, M., 1972, Microbes as tracers of water movement: Water Research, Vol. 6, pp. 731-739.

Wood, W. W., and Ehrlich, G. G., 1978, Use of baker's yeast to trace microbial movement in ground water: Ground Water, Vol. 16, No. 6, pp. 398-403.

Yates, W. E., and Akesson, N. B., 1963, Fluorescent tracers for quantitative microresidue analysis: Trans. ASAE, Vol. 16, pp. 104-114.

Zuber, A., Grabczak, J., and Kolonko, M., 1979, Environmental and artificial tracers for investigating leakages into salt mines: Isotope Hydrology, I.A.E.A., Vienna, 1979, Part 1, pp. 45-63.